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ENVIRONMENTAL DURABILITY TESTING OF STRUCTURAL ADHESIVES
PART I AF-142-2/EC-3917; PL-729-3/PL-728

University of Dayton Research Institute
Dayton, Ohio 45469

DECEMBER 1978

Interim Technical Report January 1976 - December 1977

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AIR FORCE MATERIALS LABORATORY
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A program has been conducted to investigate the durability of two modified epoxy adhesives in an elevated temperature, high humidity environment while under stress.

The results indicate that, for shear stress levels low enough to preclude fracture of the adherend surface oxide layer, and for aging times of less than 2400 hours, no significant difference exists in the time-to-failure behavior of the two adhesives. At (over)

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20. Abstract (Concluded)

higher stress levels, however, where fracture of the adherend surface oxide layer is likely, the adhesive system containing a rubber-filled primer (PL-729/PL-728) produced significantly longer times-to-failure than the adhesive system containing a non-rubber-filled primer (AF-143/EC-3917). The reason for this difference is the apparent ability of the filled primer to better tolerate the stress concentrations present around fractures of the oxide surface layer.

Evidence was also developed to indicate that the presence of the rubber filler in the PL-728 primer gives rise to a thin boundary layer along the adherend oxide surface along which fracture occurs on specimens in which the adherends have been phosphoric acid anodized. On optimized FPL etched adherends the PL-729/PL-728 system produces predominately but not exclusively cohesive failures. The AF-143/EC-3917 system produced exclusively cohesive failures within the adhesive layer for all surface treatments.

The stressed environmental agings did not degrade the residual strength of bonded specimens which survived for 2400 hours.

Phosphoric acid anodizing produced higher strengths and longer times-to-failure than optimized FPL etching of the substrate adherends.

PREFACE

This report covers the work performed during the period from January, 1976 to December, 1977 under Air Force Contract F33615-76-C-5034, Project Number 7381. Some preliminary work for the investigation reported herein was accomplished under Air Force Contract F33615-74-C-5034, Project Number 7381. The work was administered under the direction of the Systems Support Division of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Mr. Weldon Scardino (AFML/MXE) acted as Project Engineer.

The Principal Investigator on this investigation was William E. Berner. The major portion of the laboratory work was conducted by John Dues, research technician.

This report was submitted by the author in March, 1978. The contractor's report number is UDR-TR-78-09.

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SECTION I

INTRODUCTION

The last few years have witnessed a widespread and dramatic growth in research and development activities pertaining to structural adhesive bonding. One of the primary aspects of this recent adhesive bonding R&D activity which distinguishes it from earlier investigations is the use of stressed rather than unstressed durability tests to evaluate the ability of adhesives, primers, and surface preparations to withstand long-term exposure to adverse environments.

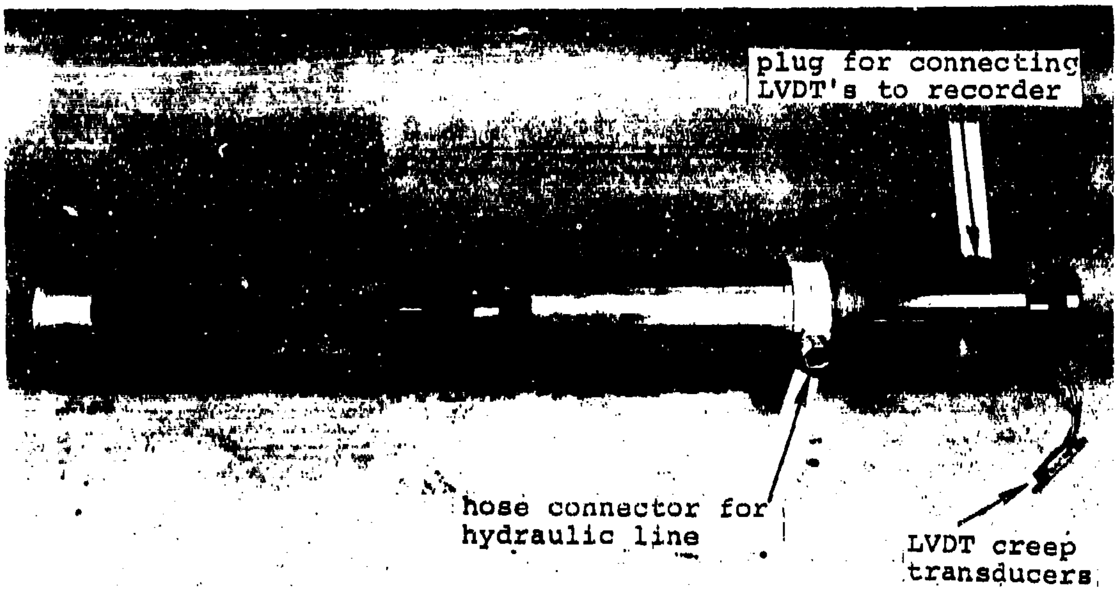
The University of Dayton Research Institute has designed, constructed, and had in service for several years, a test apparatus which permits the measurement of the durability of bonded joints while exposed to elevated temperature and humidity under a controlled stress level. This durability tester not only permits time-to-failure measurements on stressed adhesive bonds in adverse environments but also has the capability of measuring joint deformation as a function of exposure time. Section II describes the durability test apparatus and subsequent sections describe the program which developed stressed environmental durability data on two structural adhesives; PL-729-3 and AF-143-2.

In the investigation reported here, the objective was to compare the durability of two 350°F (177°C) curing adhesive systems on both acid etched and anodized adherend surfaces. Static lap shear tests were conducted and environmental stress-rupture durability tests were conducted on the apparatus described above.

SECTION II

DURABILITY TEST APPARATUS

The durability test apparatus provides the capability of conducting environmental exposures on specimens subjected to a constant tensile load during the exposure period. The environment can be controlled between 95°F (35°C) and 200°F (93°C) and between 40% and 95% R.H. Loads are applied hydraulically and can be controlled to within ± 5 lbs (± 22 N) over a range from 0 to 2500 lbs (0 to 11,125 N). Figures 1 to 3 illustrate the test apparatus and specimen mounting cells. An adhesive lap shear specimen of the type used in this program is shown mounted and also lying beside the test cell. The tester can accommodate 12 specimens simultaneously. Although all 12 are exposed to the same temperature and humidity conditions, the load on each can be independently controlled. The exposure cabinet is a standard Blue M humidity cabinet, model AC-7502HA-1, which has had 12 holes cut through the door for insertion of the test cells. Each test cell permits free access of the environment to the test specimen. Small LVDT transducers are mounted in the hydraulic loading heads of each cell. These transducers permit continuous recording of specimen creep deformation during exposure. The creep measurement capability was not utilized in this investigation. Only time-to-rupture was recorded.



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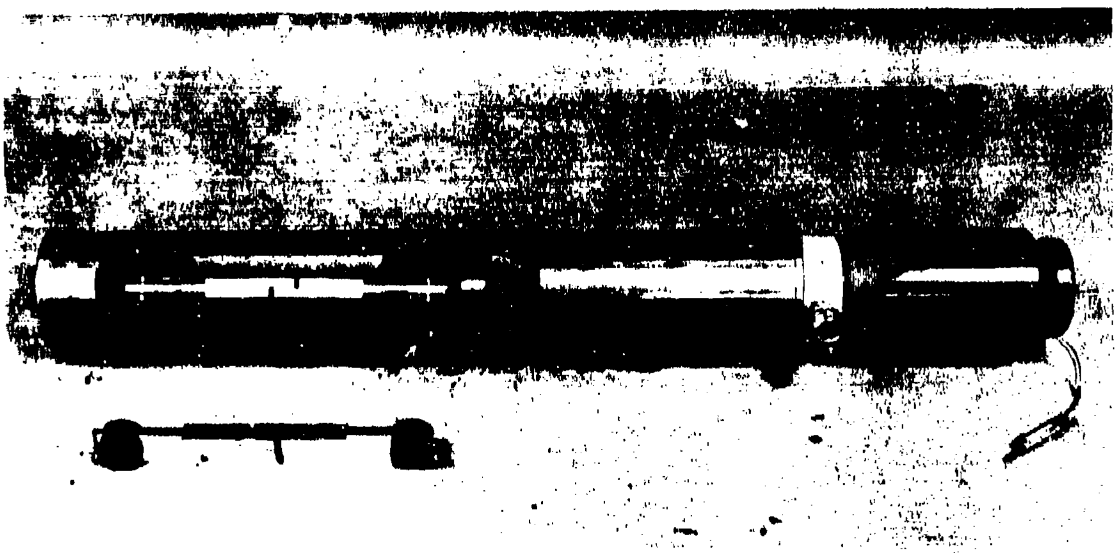
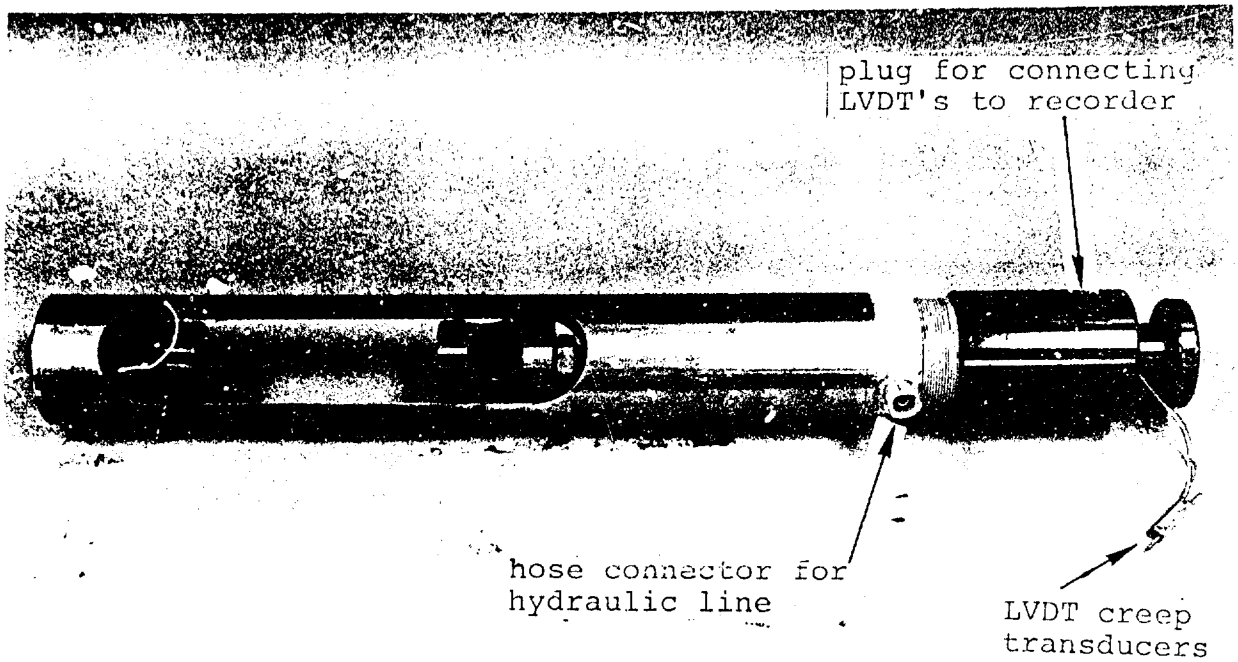


(b) Cell with mounted specimen

Figure 1. Specimen Mounting Cells For the Durability Test Apparatus.



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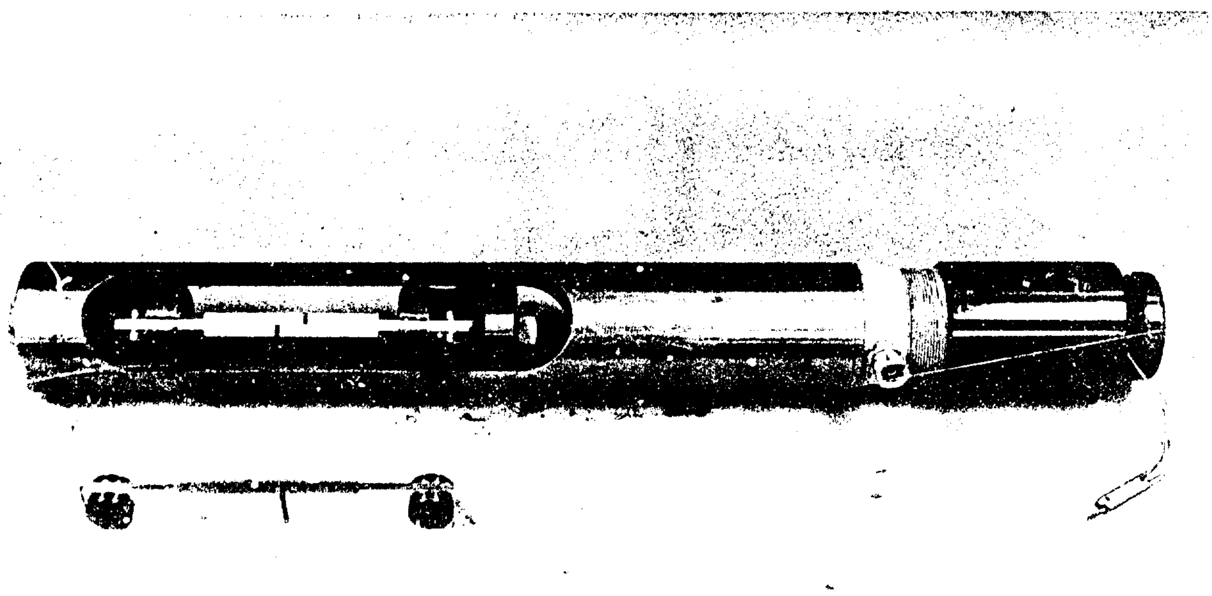

(b) Cell with mounted specimen

Figure 1. Specimen Mounting Cells For the Durability Test Apparatus.

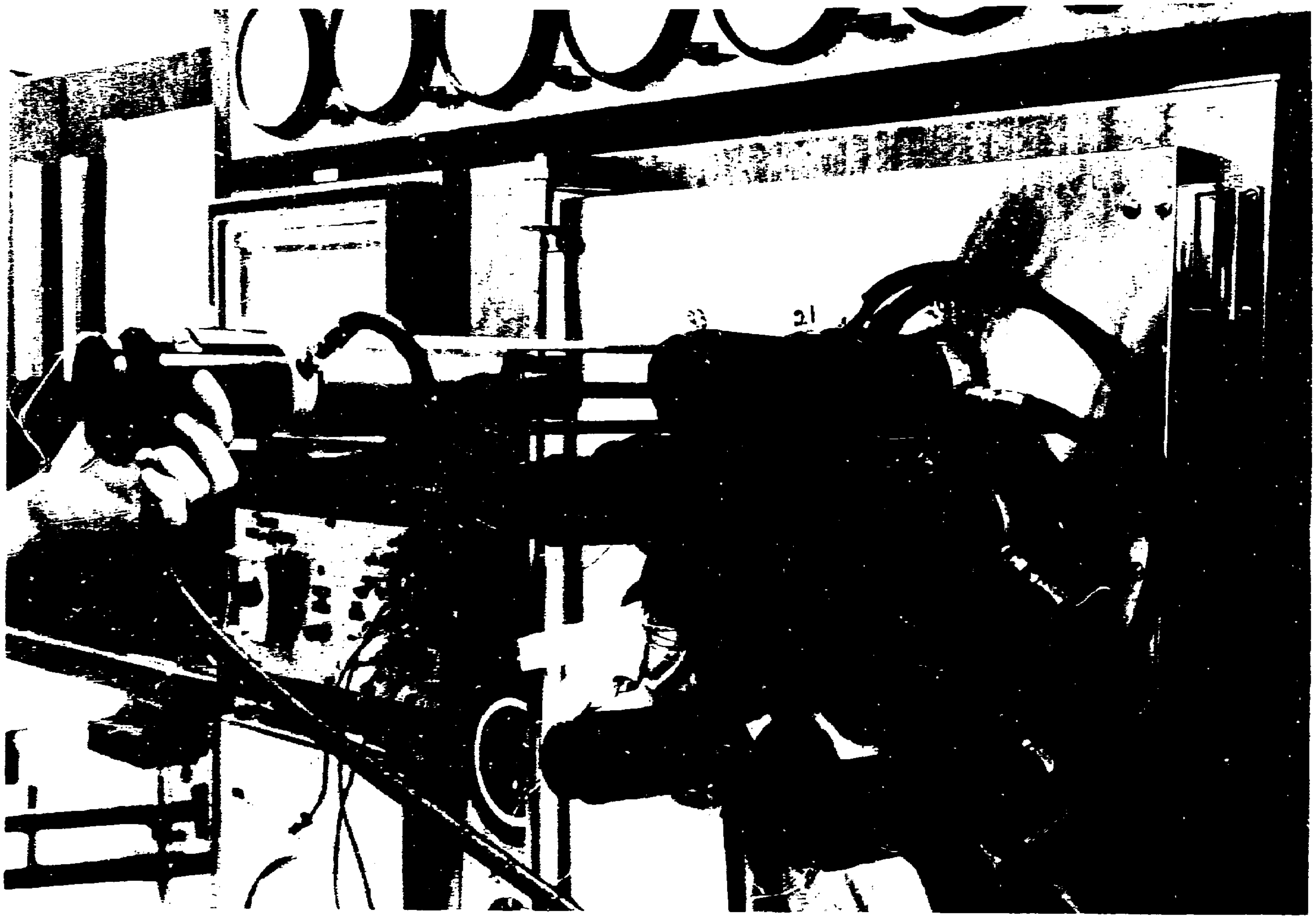

Figure 2. Specimen Mounting Cell Being Inserted Into Humidity Cabinet.

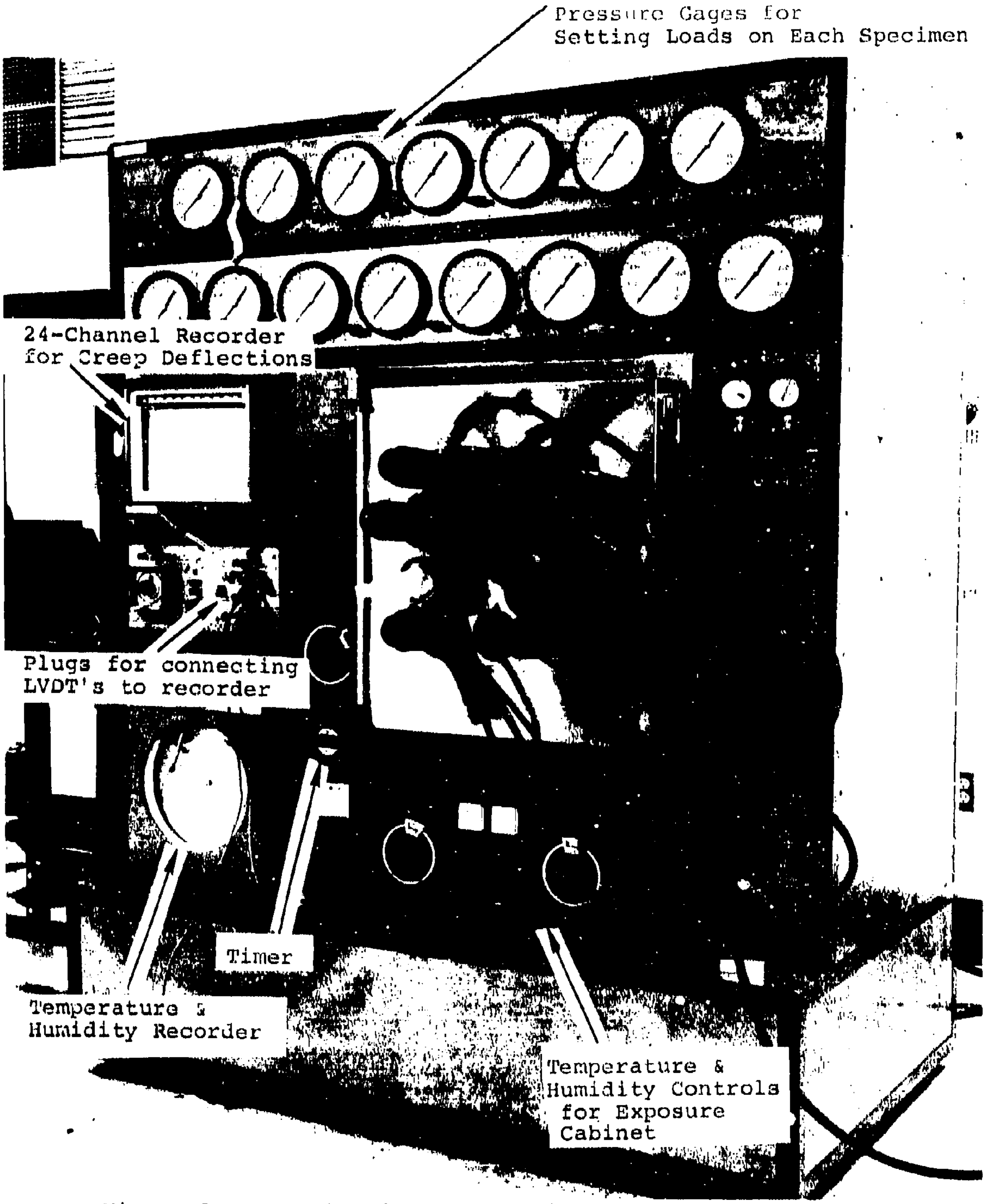

Figure 3. Overall View of Durability Test Apparatus.

SECTION III

EXPERIMENTAL PROGRAM

1. MATERIALS

Two 350°F (177°C) curing modified-epoxy structural adhesives have been evaluated; PL-729-3, by B.F. Goodrich, and AF-143-2, by 3M. Each of these two adhesives was used in combination with the adherend surface primer recommended by the manufacturer. The primer used with the PL-729-3 adhesive was PL-728, by B.F. Goodrich, and the primer used with the AF-143-2 adhesive was EC-3917, by 3M. The PL-728 primer is known to contain rubber, while the EC-3917 primer does not. Both of these are corrosion inhibiting primers.

Two types of aluminum adherends were used during the course of the investigation; 2024T3 bare and 7075T6 bare. The 2024T3 alloy was used with an optimized FPL etch* surface preparation and the 7075T6 alloy was used with a phosphoric acid anodized* surface preparation.

Two types of specimens were also utilized; the 0.063 inch (0.16 cm) thick adherend, single lap shear (SLS) specimen, and the 0.250 inch (0.65 cm) thick adherend, machined single lap shear (MSLS) specimen (also known as a blister shear specimen). Figure 4 illustrates these two specimens.

Table 1 lists the combinations of adhesive, alloy, surface preparation, and specimen type for which data were generated in this program.

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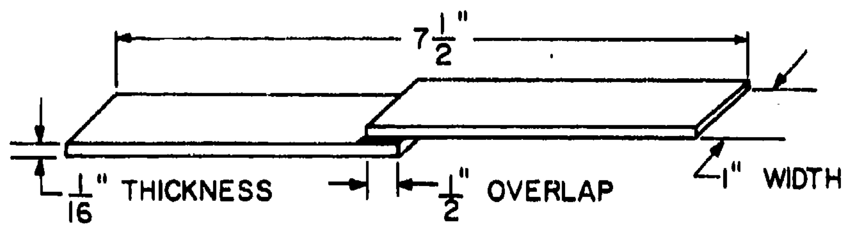
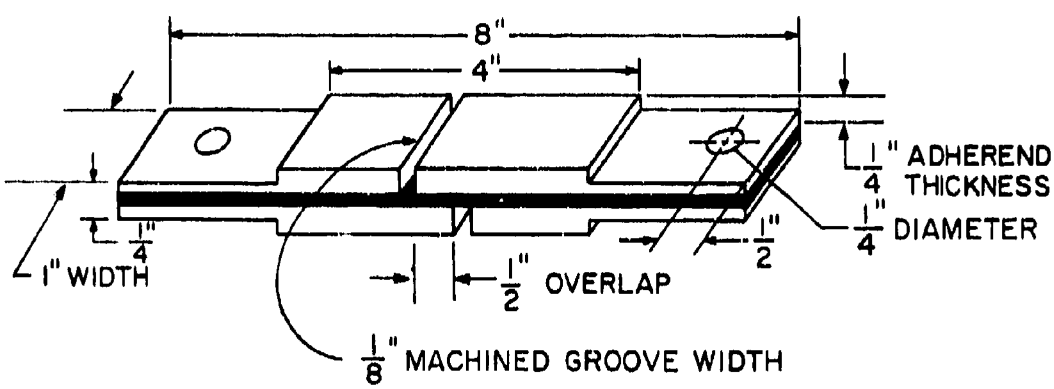
*These two surface preparations are not identical to the commonly referred preparations of the same names in use in 1977. They were based on earlier procedures which have since been revised. The essential details of the procedures used here are described in a later section of this report.



(a) 0.063 inch (0.16cm), thin adherend, single lap shear specimen



(b) 0.250 inch (0.64cm), thick adherend, machined single lap shear specimen

Figure 4. Single Lap Shear Adhesive Specimens.

TABLE 1

ADHESIVE, ALLOY, SURFACE, AND SPECIMEN COMBINATIONS TESTED

Adhesive/Primer	Adherend Alloy	Surface Preparation[1]	Specimen Type[2]
PL-729-3/PL-728	2024T3 bare	Optimized FPL etch	thin adherend, SLS
PL-729-3/PL-728	2024T3 bare	Optimized FPL etch	thick adherend, MSLS
PL-729-3/PL-728	7075T6 bare	Phosphoric Acid Anodize	thick adherend, MSLS
AF-143-2/EC-3917	2024T3 bare	Optimized FPL etch	thin adherend, SLS
AF-143-2/EC-3917	2024T3 bare	Optimized FPL etch	thick adherend, MSLS
AF-143-2/EC-3917	7075T6 bare	Phosphoric Acid Anodize	thick adherend, MSLS

[1]See process descriptions.
[2]See Figure 4.

2. SPECIMEN FABRICATION

The specimen fabrication procedure can be separated into three general phases. The first phase deals with adherend surface preparation, the second with the panel bonding operation, and the third with the machining of the bonded panel into individual test specimen. These three phases are described in some detail below. The referenced BAC numbers refer to processing specifications developed by the Boeing Aircraft Company.

a. Surface Preparation

(1) Optimized FPL Etch

The stepwise procedure used for this surface is:

1) Scrub adherend surface with a nonchlorinated detergent in tap water, rinse, and dry.
2) Wipe adherend surface with MEK and dry.
3) Vapor degrease in trichloroethylene according to BAC 5408.
4) Acid etch with the solutions and procedures contained in BAC 5514 for optimized FPL etch.

5) Rinse in continuously flowing tap water for ten minutes and dry with an air heat gun.

6) Apply primer within 1/2 hour.

(2) Phosphoric Acid Anodization

The stepwise procedure for this surface is:

1) Scrub adherend surface with a nonchlorinated detergent in tap water, rinse, and dry.

2) Wipe adherend surface with MEK and dry.

3) Vapor degrease in trichloroethylene according to BAC 5408.

4) Immerse in a deoxidizing alkaline wash of Oakite #164 at 140°F (60°C) for ten minutes.

5) Rinse with continuously flowing tap water for ten minutes.

6) Acid etch with an Oakite #34/sulfuric acid solution for one to three minutes at 72°F (22°C).

7) Rinse with continuously flowing tap water for ten minutes.

8) Phosphoric acid anodize the adherends for 25 minutes at 10 ± 1 volts.

9) Rinse with continuously flowing tap water for ten minutes and dry panels with an air heat gun.

10) Apply primer within 1/2 hour.

b. Panel Bonding

1) Layup primed panels and adhesive film into assembly required for final specimens.

2) Place layup assembly in autoclave at room temperature.

3) Pull a vacuum on the bagged assembly.

4) Apply 45 ± 5 psi (310 ± 34 KPa) over the bladder and then release the vacuum.

5) Heat the autoclave at 5-7°F/min to 350°F (177°C).

6) Hold at 350°F (177°C) for 60 minutes.

7) Cool the autoclave to below 200°F (93°C), maintaining the 45 ± 5 psi (310 ± 34 KPa) over the bladder.

8) Release pressure and remove the panel from the autoclave.

c. Specimen Preparation

(1) 0.063 Inch (0.16 Cm) Thick SLS Specimens

These panels are 9 inches (22.9 cm) wide when bonded and are cut into seven specimens by clamping them into a special slotted grip and milling them with a gang of eight aligned circular cutting blades. No further machining is needed other than the drilling of holes in the ends for pinning into the test grips.

(2) 0.250 Inch (0.64 Cm) Thick MSLS Specimens

These panels are 16 inches (40.6 cm) wide when bonded and are first cut into 13 individual specimens on a bandsaw. These rough-cut specimens are then finish milled down to their final 1 inch (2.54 cm) wide by 7 inches (17.8 cm) long dimension. Holes are then drilled into the ends for mounting into the test grips as well as for specimen location in a machining fixture when the specimens are slotted across their width. The slots are cut across the specimens to provide the lap joint. These slots are machined down to, but not through, the adhesive layer. The ends of the specimen are then machined down to a 0.250 inch (0.64 cm) thickness to fit into the test grips on the environmental stress-rupture durability tester.

3. TEST PLAN

Three types of tests were conducted on the lap shear specimens in this investigation. The first type was a simple static test on the as-fabricated dry specimens at three different temperatures; 72°F (22°C), 140°F (60°C), and 250°F (121°C). The second was also a simple static test at 72°F (22°C) on specimens which had been exposed to elevated temperature, high humidity aging (140°F/60°C and 100% R.H.) for 28 and 100 days prior to testing. The third type of test was an environmental stress-rupture test in which the lap shear specimens were loaded to various stress levels and exposed to a 140°F (60°C), 95-100% R.H. environment until failure. If no failure had occurred

within 2400 hours, the specimens were removed from the environmental durability tester and tested statically at 72°F (22°F) for residual strength. The stresses imposed during the environmental durability exposures varied between 20% and 80% of the ultimate strength obtained in the dry static tests at either 72°F (22°C) or 140°F (60°C). All of the lap shear tests conducted on specimens which had been humidity aged (either the static or residual strength tests) were completed within 30 minutes after the specimen was removed from the environmental chamber. Additionally, each of these specimens were wrapped with a wet cloth to prevent drying during this period.

SECTION IV

DISCUSSION OF RESULTS

Tables 2-13 present the test results obtained during this investigation. Tables 2-7 represent data generated for the AF-143-2/EC-3917 adhesive/primer system, while Tables 8-13 represent data generated for the PL-729-3/PL-728 adhesive/primer system. The even-numbered tables present the average ultimate strength values obtained in the static lap shear tests. The odd-numbered tables present the average results of the environmental stress-rupture durability tests. Complete tabulations of all the individual test data, including computed standard deviations, for both the static and environmental durability tests are presented in Appendix A. In addition to these tabulations, the environmental stress-rupture durability data are graphically illustrated in Figures 5 through 10.

1. STATIC LAP SHEAR TEST RESULTS

It is readily apparent that the thick adherend MSLS type specimens have a substantially higher static failure strength than the thin adherend SLS type specimens and are also capable of sustaining higher stresses for longer periods of time during environmental exposure. This is undoubtedly due to the greater bending resistance of the thicker adherends, with concomitant reduction of peeling stresses in the bondline. It is also evident that the specimens with 7075 alloy adherends fail at slightly higher loads and exhibit slightly longer time-to-failure during environmental stress-rupture than the specimens with 2024 alloy adherends. Since the failure modes were cohesive, any difference in the nature of the oxide produced by the surface preparations on these two different alloys would not have accounted for this difference. It is probably due to reduced peel stresses because of the higher yield stress of the 7075T6 alloy.

TABLE 2

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917

Test Temperature (°F)	Test Temperature (°C)	Pre-Test Conditioning [days@140°F(60°C) and 100% R.H.; No Load]	Ultimate Strength (psi)	Ultimate Strength (MPa)	Failure Mode (% Coh. Failure)	Number of Specimens Represented
72	22	None	3020	20.8	100	5
140	60	None	2980	20.5	100	11
250	121	None	2570	17.7	100	5
72	22	28	3050	21.0	100	5
72	22	100	2790	19.2	100	5

TABLE 3

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 72°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Str.[2] (psi)	(MPa)	Failure Mode (%Coh.)	Number of Specimens Represented
2420	16.7	80	0.68	---	---	100	3
2110	14.6	70	1650	3250[3]	22.4	100	3
1810	12.5	60	2400[1]	3010	20.8	100	3
1510	10.4	50	2400[1]	3090	21.3	100	3
600	4.1	20	2400[1]	2880	19.9	100	3

[1] Joints did not fail within 2400-hour exposure period and were removed for residual strength testing.

[2] All residual strengths were obtained at 72°F (Section III.3).

[3] Two specimens survived 2400-hour exposure period.

TABLE 4

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days@140°F(60°C) and 100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh. Failure)	Number of Specimens Represented
72	22	None	5500	37.9	90	10
140	60	None	4900	33.8	90	5
250	121	None	3990	27.5	100	5
72	22	28	5730	39.5	90	5
72	22	100	4760	32.8	75	3

TABLE 5

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Str.[2] (psi)	(MPa)	Failure Mode (%Coh.)	Number of Specimens Represented
3920	27.0	80	2.6	---	---	100	3
3430	23.7	70	340	---	---	100	4
3180	21.9	65	480	---	---	100	4
2940	20.3	60	1043	---	---	100	3
1960	13.5	40	2400[1]	5720	39.4	100	3
980	6.8	20	2400[1]	5470	37.7	100	3

[1] Joints did not fail within 2400-hour exposure period and were removed for residual strength testing.

[2] All residual strengths were obtained at 72°F (Section III.3).

TABLE 6

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 7075T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: AF-143-2/EC-3917

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days@140°F(60°C) and 100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh. Failure)	Number of Specimens Represented
72	22	None	6330	43.6	85	6
140	60	None	5180	35.7	95	10
250	121	None	4360	30.0	100	6
72	22	30	5970	41.2	100	6
72	22	100	5780	39.8	100	5

TABLE 7

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 7075T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: AF-143-2/EC-3917
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Str.[2] (psi)	(MPa)	Failure Mode (%Coh.)	Number of Specimens Represented
3630	25.0	70	480	---	---	100	3
3110	21.4	60	1530	---	---	100	3
2590	17.6	50	2400[1]	4270	29.5	100	2
2070	14.3	40	2400[1]	5900	40.7	100	3
1550	10.7	30	2400[1]	5760	39.7	100	3
1040	7.2	20	2400[1]	5840	40.3	100	3

[1] Joints did not fail within 2400-hour exposure period and were removed for residual strength testing.

[2] All residual strengths were obtained at 72°F (Section III.3).

TABLE 8

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days@140°F(60°C) and 100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh. Failure)	Number of Specimens Represented
72	22	None	3920	27.0	100	5
140	60	None	3910	27.0	100	11
250	121	None	3380	23.3	100	5
72	22	28	3050	21.0	100	5
72	22	100	*	*	*	0

*Did not run 100 day agings.

TABLE 9

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 72°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Str.[2] (psi)	(MPa)	Failure Mode (%Coh.)	Number of Specimens Represented
2740	18.9	70	510	---	---	100	5
2350	16.2	60	1990	3720[3]	25.6	100	3
1960	13.5	50	2400[1]	4000	27.6	100	3
780	5.4	20	2400[1]	3700	25.5	100	3

[1]Joints did not fail within 2400-hour exposure period and were removed for residual strength testing.

[2]All residual strengths were obtained at 72°F (Section III.3).

[3]Two specimens survived 2400-hour exposure period.

TABLE 10

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days@140°F(60°C) and 100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh. Failure)	Number of Specimens Represented
72	22	None	6370	64.6	100	10
140	60	None	5780	39.9	100	5
250	121	None	4770	32.9	100	5
72	22	28	6560	45.2	85	5
72	22	100	6350	43.8	95	3

TABLE 11

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Str.[2] (psi)	(MPa)	Failure Mode (%Coh.)	Number of Specimens Represented
4630	31.9	80	21.0	---	---	100	3
4050	27.9	70	470	---	---	95	3
3760	25.9	65	820	---	---	90	3
3470	23.9	60	810	---	---	70	3
2330	16.1	40	1860	5630[3]	38.8	55	3
1160	4.0	20	2400[1]	6660	45.9	90	3

[1] Joints did not fail within 2400-hour exposure period and were removed for residual strength testing.

[2] All residual strengths were obtained at 72°F (Section III.3).

[3] Two specimens survived 2400-hour exposure period.

TABLE 12

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 7075T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: PL-729-3/PL-728

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days@140°F(60°C) and 100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh. Failure)	Number of Specimens Represented
72	22	None	6570	45.3	0[1]	6
140	60	None	6280	43.3	0[1]	11
250	121	None	4500	31.0	0[1]	6
72	22	30	7190	49.6	0[1]	6
72	22	100	7290	50.3	0[1]	6

[1]Failures were cohesive within the primer layer and very near the adherend/primer interface.

TABLE 13

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 7075T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: PL-729-3/PL-728
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Str.[4] (psi)	(MPa)	Failure Mode (%Coh.)	Number of Specimens Represented
3770	26.0	60	1670[1]	6430	44.3	0[5]	3
3140	21.6	50	1700[2]	6220	42.9	0[5]	1
2510	17.3	40	2400[3]	7070	48.7	0[5]	3
1880	13.0	30	2400[3]	7180	49.5	0[5]	3
1260	8.7	20	2400[3]	6970	48.1	0[5]	3

[1]Two of the three specimens did not fail during environmental stress-rupture exposure; one was removed after 1800 hours and one after 2400 hours for residual strength testing.

[2]Joint did not fail and was removed after 1700 hours for residual strength testing.

[3]Joints did not fail and were removed after 2400 hours for residual strength testing.

[4]All residual strengths were obtained at 72°F (Section III.3).

[5]Failures were cohesive within the primer layer and very near the adherend/primer interface.

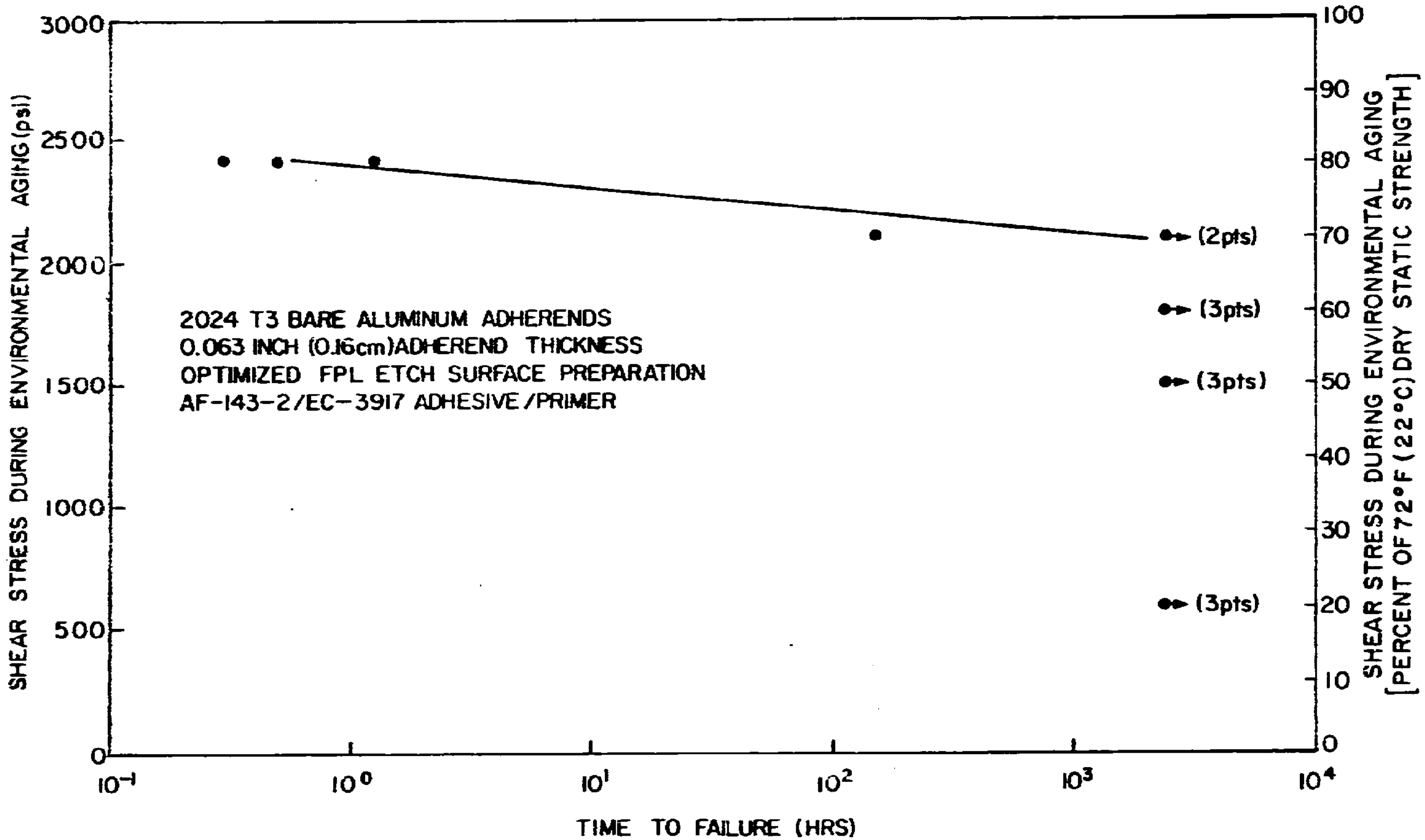


Figure 5. Environmental Stress-Rupture Time-to-Failure Behavior of Single Lap Shear (SLS) Adhesive Joints at 140°F (60°C) and 95-100% R.H.

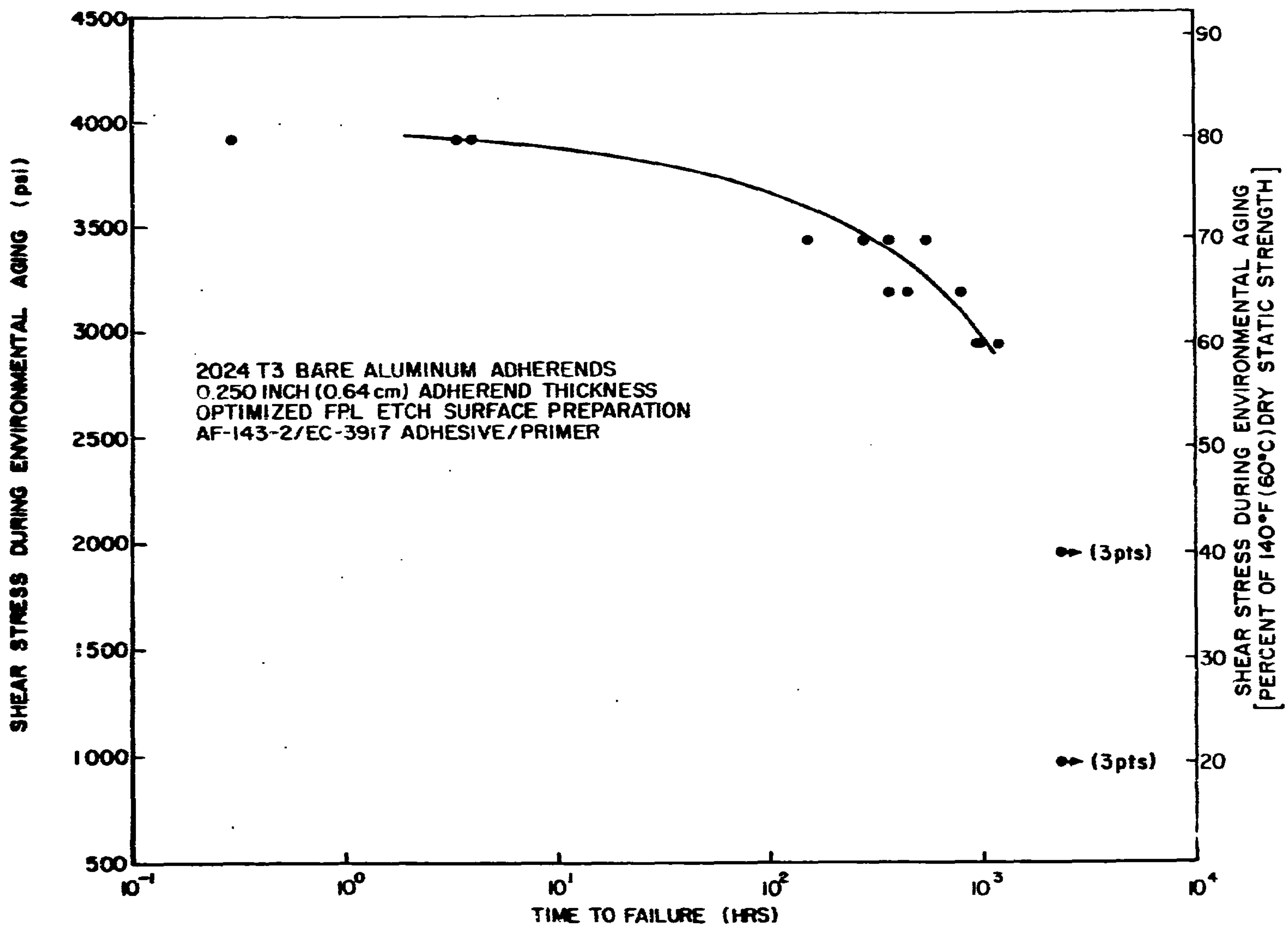


Figure 6. Environmental Stress-Rupture Time-to-Failure Behavior of Machined Single Lap Shear (MSLS) Adhesive Joints at 140°F(60°C) and 95-100% R.H.

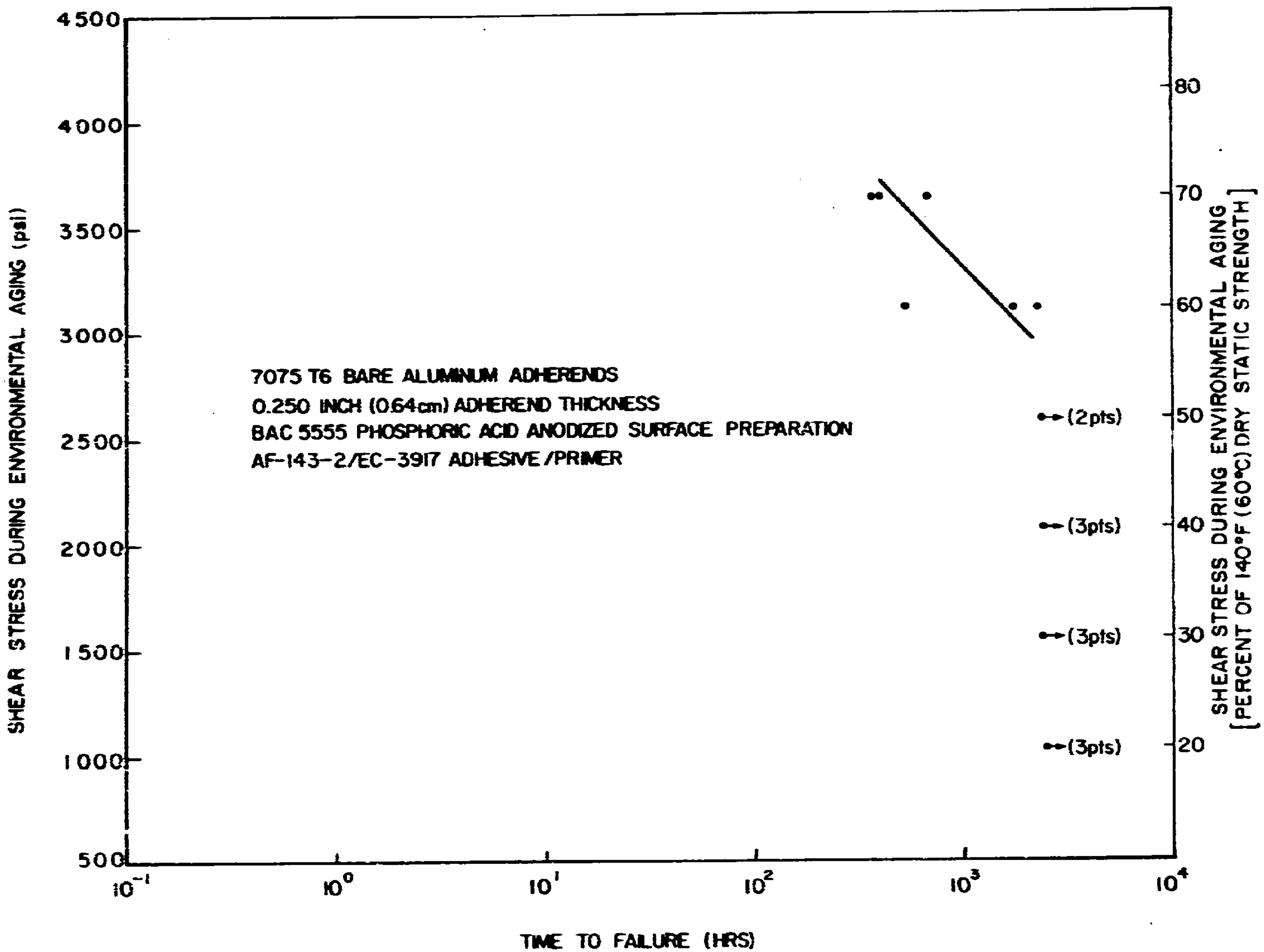


Figure 7. Environmental Stress-Rupture Time-to-Failure Behavior of Machined Single Lap Shear (MSLS) Adhesive Joints at 140°F(60°C) and 95-100% R.H.

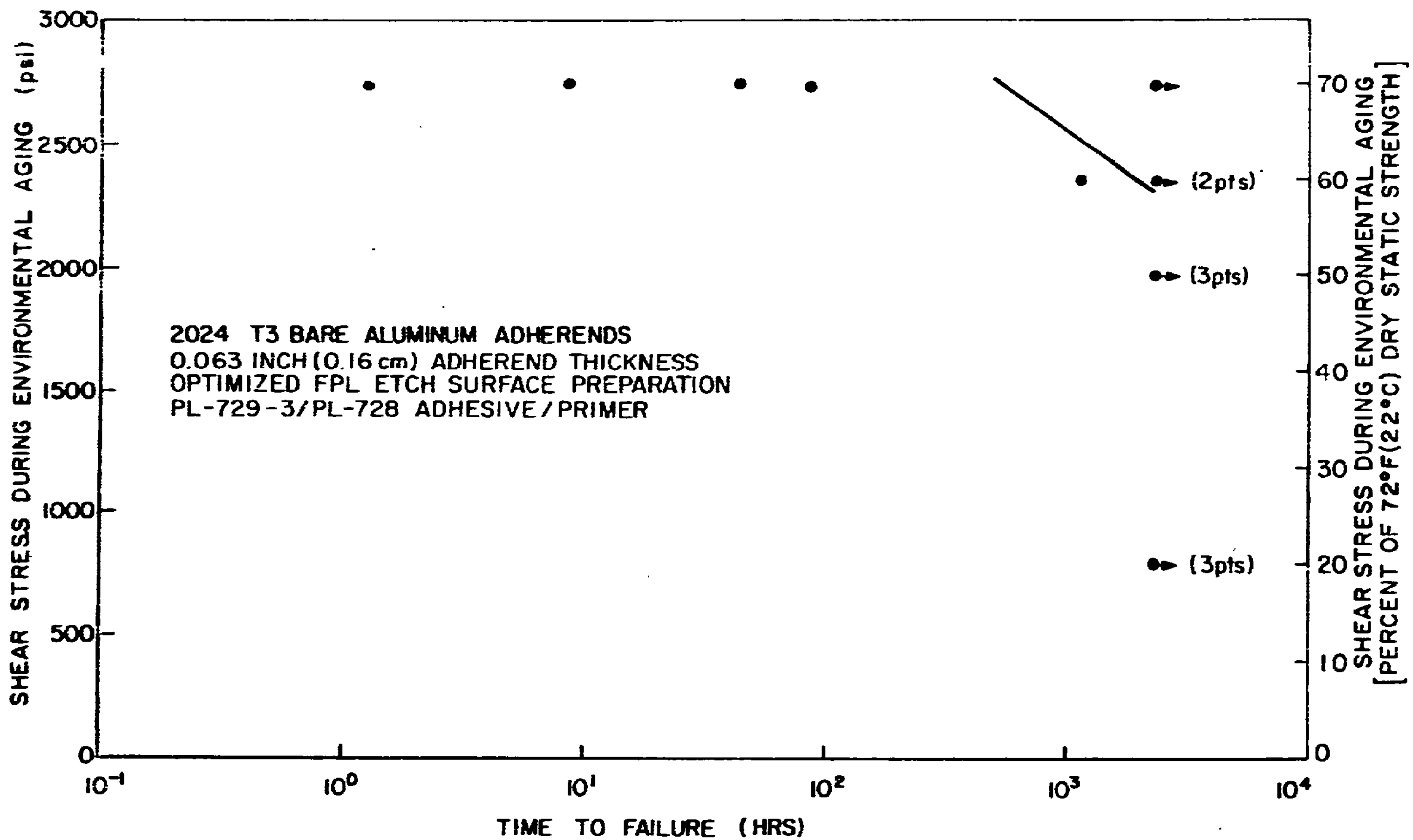


Figure 8. Environmental Stress-Rupture Time-to-Failure Behavior of Single Lap Shear (SLS) Adhesive Joints at 140°F (60°C) and 95-100% R.H.

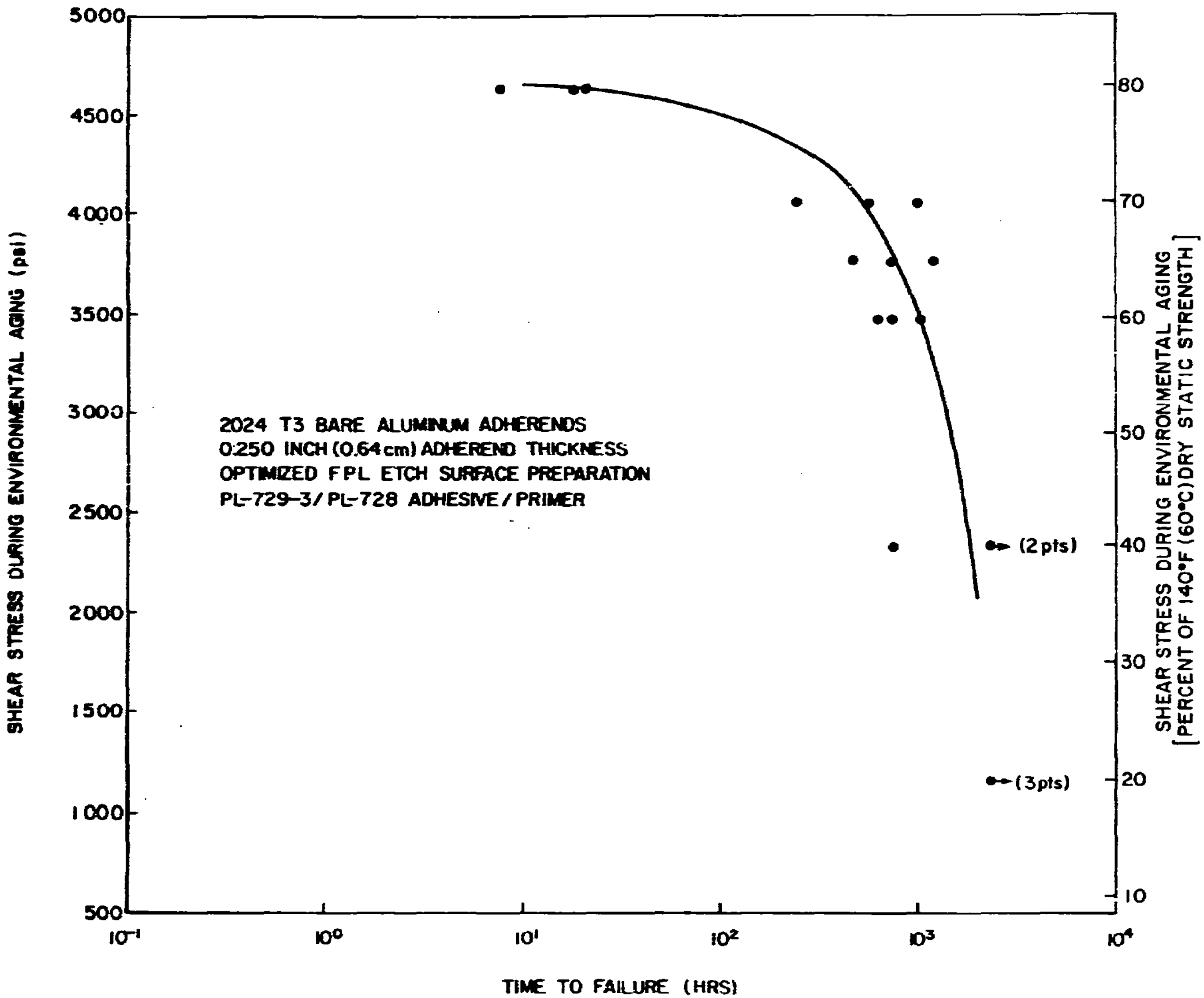


Figure 9. Environmental Stress-Rupture Time-to-Failure Behavior of Machined Single Lap Shear (MSLS) Adhesive Joints at 140°F(60°C) and 95-100% R.H.

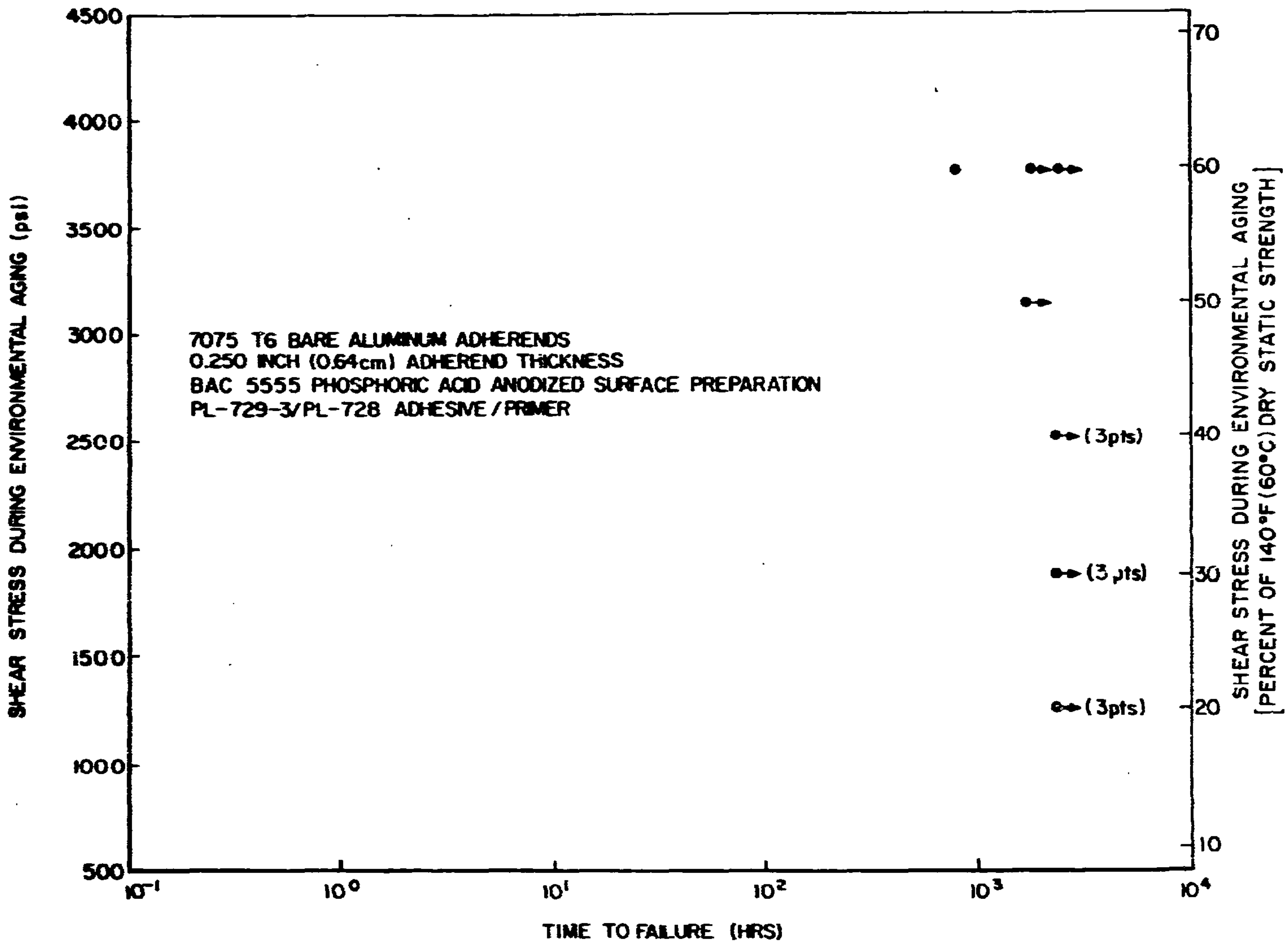


Figure 10. Environmental Stress-Rupture Time-to-Failure Behavior of Machined Single Lap Shear (MSLS) Adhesive Joints at 140°F(60°C) and 95-100% R.H.

Bonds made with PL-729-3 adhesive exhibited consistently higher static lap shear strengths than those made with AF-143-2. This difference amounted to 15-20% on the MSLS specimens and about 30% on the SLS specimens, when one compares totally cohesive failures. Both adhesives seem to lose about the same percentage of strength with increasing test temperature.

Twenty-eight day humidity agings prior to static testing have little effect on the R.T. strength of either of the two adhesives investigated. After 100 day humidity agings, however, there is a slight difference between the behavior of the two adhesives. The PL-729-3 adhesive joints, after 100 days' aging exhibit about the same R.T. strength as dry unaged specimens, but the AF-143-2 adhesive joints exhibit a slight ($\sim$10%), but still noticeable, loss in strength. Since these AF-143-2 failures after 100 days' aging are still predominantely cohesive in nature, this reduction in strength seems to reflect a slight degradation of the adhesive itself rather than the interfacial adhesive bond.

An interesting point to note is the comparative failure modes of the two adhesive systems. The AF-143/EC-3917 adhesive/primer systems exhibited predominantely cohesive failures for all test conditions. The PL-729/PL-728 adhesive/primer system, on the other hand, exhibited predominantely cohesive failure (as evident to visual inspection) only on the optimized FPL etched surfaces. On the phosphoric acid anodized surface, this adhesive system exhibited what appears to be adhesive failures. One failure surface was gray in color (the color of the substrate adherend) and the other was yellow (the color of the adhesive). An ESCA analysis of these failure surfaces was conducted to try to determine if the apparent interfacial adhesive failure was indeed interfacial, or whether a thin residual film of primer remained on the gray adherend surface.

It was found that the chemical species, and their relative amounts, present on the gray colored surface as well as on the

yellow colored surface correspond to the composition of the PL-728 primer. This would indicate that a thin film of primer did in fact remain on the adherend surface and that the failure was not adhesive, along the interface, but cohesive, within the primer layer. This cohesive failure within the primer layer occurred very near to the adherend surface. Since a freshly primed surface, prior to bonding, is thick enough to impart a yellowish color to the surface, the layer left after fracture is evidently so thin that it is insufficient to alter the color of the substrate.

Marceau* has speculated on why failure occurs at this location and his hypothesis seems to explain these results also. Essentially, his reasoning is that the fine columnar porous structure of the phosphoric acid anodized surface is such that the larger molecules in the adhesive (the rubber molecules) cannot penetrate into the oxide while the shorter molecules in the adhesive mix can. This molecular segregation results in a boundary layer along which failure is most likely to occur.

Although in Marceau's study, such a boundary layer resulted in failures at considerably lower strength levels, this was not the case here.

The reason for this difference between the results of the two studies probably is twofold. First, Marceau utilized the same adhesive and primer throughout his study, with the only variable material parameter being the presence or absence of rubber in the primer. In this study the adhesives and primers are both different and differences in their physical and chemical characteristics can be influencing the results as well as simply the presence or absence of rubber in the

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*J.A. Marceau, "An SEM Analysis of Adhesive Primer Oriented Bond Failures on Anodized Aluminum," presented at 23rd National SAMPE Symposium, Anaheim, Calif., May 2-4, 1978.

primer. Second, in this investigation, the phosphoric anodized surfaces were on 7075T6 bare aluminum, while the optimized FPL etched surfaces were on 2024T3 bare aluminum. Since the 7075T6 alloy produces higher strengths than the 2024T3 alloy, any weakness in the adherend/primer boundary layer on anodized surfaces produced by molecular segregation is somewhat, if not completely, offset by the alloy differences. The difference in static lap shear strength between the PL-729/PL-728 system and the AF-143/EC-3917 system was, in fact, less on the anodized surface than on the acid etched surface, implying that the presence of rubber in the PL-728 primer did actually reduce the strength levels obtained on the anodized adherends in spite of the other variables influencing these results. At any rate, the applicability of Marceau's hypothesis concerning failure location to the results observed here is felt to be very reasonable.

2. ENVIRONMENTAL STRESS-RUPTURE TEST RESULTS

During environmental stress-rupture testing, the 7075T6 alloy produces longer times-to-failure than the 2024T3 alloy. As indicated before with regard to the static lap shear data, this is probably due to the higher yield strength of the 7075T6 alloy and the reduction in peeling stresses.

Of particular interest is the comparative behavior of the AF-143 and PL-729 adhesive systems during environmental stress-rupture testing. To facilitate this comparison, the stress vs. time-to-failure curves shown in Figures 6, 7, 9, and 10 for the thick adherend MSLS type specimens are replotted in Figure 11. It can be seen from this figure that the PL-729/PL-728 adhesive/primer system produces longer times-to-failure than the AF-143/EC-3917 adhesive/primer system for applied lap shear stresses above about 2800 psi (1.93 MPa). Below 2800 psi (1.93 MPa) it would appear that both adhesive systems produce similar times-to-failure. This behavior pattern seems to hold for both types of alloy/surface treatment, the only difference

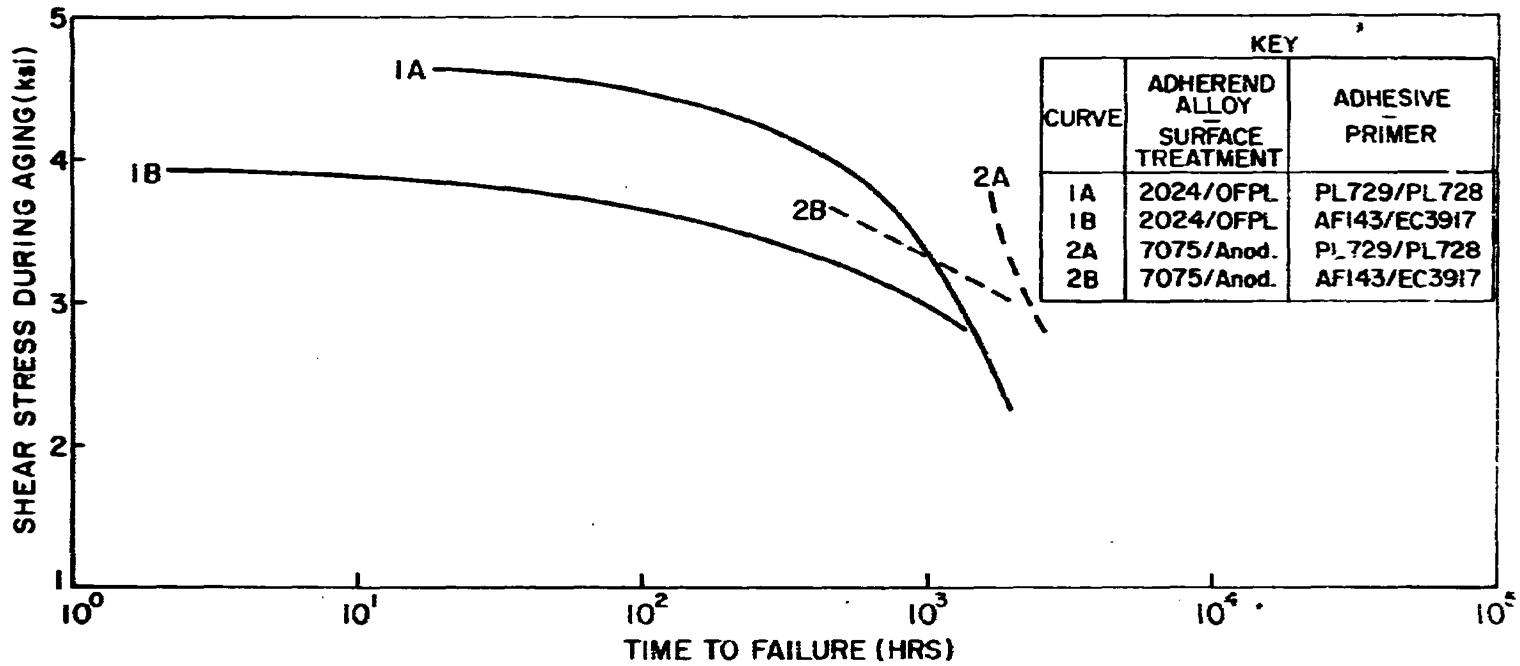

Figure 11. Comparative Environmental Stress-Rupture Time-to-Failure Behavior of Machined Single Lap Shear (MSLS) Adhesive Joints at 140°F(60°C) and 95-100% R.H.

being that the curves are shifted out to longer failure times for the 7075/anodized combination.

The reason for this type of behavior may also be explained by one of the hypotheses presented in the paper by Marceau* mentioned earlier. The reasoning behind this explanation is that when the aluminum adherend is sufficiently strained during specimen loading, the surface oxide layer, being of a much higher modulus and much lower ultimate strain capability, will fracture. These oxide fractures "produce stress risers at the oxide-adhesive interface where the adhesive bridges cross the oxide fracture." Since the PL-728 primer is rubber filled while the EC-3917 is not, it may well be "tougher" and capable of tolerating these stress risers better than the EC-3917 primer. If the strain in the oxide layer is sufficient at 2800 psi (1.93 MPa) and above to cause these fractures, the cracks may be propagated into the EC-3917 primer, and thence into the AF-143 more readily than they are propagated into the toughened PL-728 primer and the PL-729 adhesive, resulting in the longer times-to-failure at high stress levels observed in Figure 11. This may also explain the higher static lap shear properties exhibited by the PL-729/PL-728 system. Some simple calculations at this point can indeed verify that for the types of specimens used, the strains in the oxide layer when the lap joint is at 2800 psi (1.93 MPa) or above are sufficient to cause oxide fracture. These calculations are presented in Appendix C. Although it would appear then, from these results, that the fracture of the surface oxide layer is more significant in affecting joint strength and durability at high stress levels than the presence or absence of a rubber filler in the primer, one must keep in mind the material variables discussed in Section IV.1 which are simultaneously influencing the results.

Below 2800 psi (1.93 MPa), where oxide fracture does not occur, there seems to be little difference in the lifetimes produced by the two adhesive systems. For this situation,

the only apparent degradative influence upon the life of the joints would appear to be the hot, humid environment. The results of the tests conducted in this program, therefore, do not show much difference in the environmental stress-rupture durability of the two adhesives at stresses below 2800 psi (1.93 MPa).

It is readily apparent from the data in Tables 2-13 that the residual strength of the specimens which survive the 2400-hour durability tests are not degraded by the exposure. Neither does the stress level during exposure affect the residual strength. Just as with the static test results, the residual strength of the 7075T6 specimens is slightly higher than that of the 2024T3 specimens and the residual strength of the PL-729-3 specimens is slightly higher than that of the AF-143-2 specimens.

SECTION V
CONCLUSIONS

1. Environmental stress-rupture tests conducted at shear stress levels low enough to preclude fracture of the adherend surface oxide layer [below 2800 psi (1.93 MPa)] indicated no significant difference in the time-to-failure behavior of either of the two adhesives evaluated in this investigation. Observations were only carried out to 2400 hours, however, and such differences may have been observed if longer tests had been conducted.

2. Environmental stress-rupture tests conducted at shear stress levels high enough to cause fracture of the adherend surface oxide layer [above 2800 psi (1.93 MPa)] indicated a significant difference in the time-to-failure behavior of the two adhesives evaluated in this investigation. The adhesive system incorporating a rubber modified primer (PL-729/PL-728) survived considerably longer than the system incorporating a primer without rubber (AF-143/EC-3917). The reason for this greater time-to-failure is apparently due to the ability of the rubber toughened primer to tolerate stress risers at the surface oxide cracks better than the primer without the rubber toughening agent.

3. A marked difference in failure modes between the two adhesives was observed in the environmental stress-rupture results. The AF143 failed exclusively by a cohesive failure mode within the adhesive layer. The PL729 system, on the other hand, exhibited some adhesive failure at the adherend interface on the OFPL etched surfaces. On the PAA surfaces, the PL729 system failed exclusively within the primer layer. The significance of these comparative failure modes must be assessed alongside the comparative strength levels and durability of the two adhesive systems by the individual user to determine which may be more important to their particular application. The reasons for this difference in failure mode are discussed in the text.

4. The phosphoric acid anodized surface treatment produces consistently higher static properties and longer times-to-failure during environmental stress-rupture testing than the optimized FPL etch surface treatment for both adhesive systems.

5. The PL-729/PL-728 adhesive system exhibited consistently higher static lap shear strengths than the AF-143/EC-3917 adhesive system although the difference was more pronounced on acid etched surfaces than it was on phosphoric acid anodized surfaces. The reason for this surface influence is due to the different failure mode observed on phosphoric acid anodized surfaces bonded with PL-729/PL-728.

6. Both adhesive systems lose about the same percentage of their dry room temperature lap shear strength at elevated temperature.

7. Unstressed, elevated temperature, high humidity aging has no adverse effect on the room temperature strength of the PL-729/PL-728 adhesive system. Similar aging has no adverse effect on the room temperature strength of the AF-143/EC-3917 adhesive system for 28 day aging periods, but after 100 day agings the strength of this system falls by about 10%.

8. If good interfacial bonding is achieved (typified by predominately or completely cohesive failure modes), 7075T6 bare aluminum alloy adherends produce higher strengths and longer durability than the 2024T3 bare aluminum alloy adherends. This is apparently due to the fact that the higher yield stress of the former alloy reduces the peeling stresses introduced into the adhesive in a single lap shear specimen.

SECTION VI
RECOMMENDATIONS FOR FURTHER STUDY

1. The apparent fracture of the surface oxide layer at high stress levels and the concurrent effect of this phenomena upon the durability and strength of adhesive joints prepared with a rubber filled primer vs. a non-rubber filled primer, indicate an important aspect of bond joint durability which must be considered in the selection of materials, joint design, and the design of future experimental programs to investigate adhesive joint durability.

2. Since the two alloys used as adherends in this investigation have different mechanical properties, leading, all other things being equal, to different lap shear strengths and environmental stress-rupture lifetimes, it would be advisable to eliminate this material variable in future studies. Further, the nature of the oxide produced by the surface treatment may be different on each alloy.

APPENDIX A

COMPLETE TEST DATA

TABLE A.1

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days @ 140°F(60°C) and 95-100% R.H. No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh.Failure)
72	22	None	3040	20.9	100
72	22	None	3000	20.7	100
72	22	None	3020	20.8	100
72	22	None	2960	20.4	100
72	22	None	3080	21.2	100
Average			3020	20.8	100
Std. Dev.			45	0.3	0
140	60	None	2990	20.6	100
140	60	None	3150	21.7	100
140	60	None	3040	20.9	100
140	60	None	3050	21.0	100
140	60	None	2980	20.5	100
140	60	None	2840	19.6	100
140	60	None	2980	20.5	100
140	60	None	2880	19.9	100
140	60	None	2960	20.4	100
140	60	None	2960	20.4	100
140	60	None	2980	20.5	100
Average			2980	20.5	100
Std. Dev.			82	0.6	0
250	121	None	2760	19.0	100
250	121	None	2370	16.3	100
250	121	None	2560	17.6	100
250	121	None	2550	17.6	100
250	121	None	2620	18.1	100
Average			2570	17.7	100
Std. Dev.			140	1.0	0
72	22	28	3270	22.5	100
72	22	28	3300	22.8	100
72	22	28	3060	21.1	100
72	22	28	2830	19.5	100
72	22	28	2780	19.2	100
Average			3050	21.0	100
Std. Dev.			243	1.7	0
72	22	100	2690	18.5	100
72	22	100	2760	19.0	100
72	22	100	2910	20.0	100
72	22	100	2620	18.0	100
72	22	100	2990	20.6	100
Average			2790	19.2	100
Std. Dev.			154	1.1	0

TABLE A.2

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days @ 140°F(60°C) and 95-100% R.H. No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh.Failure)
72	22	None	5560	38.3	100
72	22	None	5700	39.3	100
72	22	None	5660	39.0	50
72	22	None	5590	38.5	80
72	22	None	5670	39.1	100
72	22	None	5560	38.3	100
72	22	None	4890	33.7	75
72	22	None	5930	40.9	100
72	22	None	5470	37.7	100
72	22	None	4920	33.9	100
Average			5495	37.9	90
Std. Dev.			334	2.3	0
140	60	None	5210	35.9	100
140	60	None	4810	33.1	100
140	60	None	4790	33.0	50
140	60	None	5080	35.0	100
140	60	None	4570	31.5	100
Average			4900	33.8	100
Std. Dev.			251	1.7	0
250	121	None	4340	29.2	100
250	121	None	4090	28.2	100
250	121	None	3390	23.4	100
250	121	None	4200	29.0	100
250	121	None	3910	27.0	100
Average			3990	27.5	100
Std. Dev.			368	2.5	0
72	22	28	5950	41.0	100
72	22	28	5870	40.5	100
72	22	28	5730	39.5	50
72	22	28	5560	38.3	100
72	22	28	5540	38.2	100
Average			5730	39.5	90
Std. Dev.			182	1.3	0
72	22	100	5630	38.8	100
72	22	100	3450	23.8	20
72	22	100	5190	35.8	100
Average			4760	32.8	75
Std. Dev.			1152	7.9	46

TABLE A.3

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 7075 T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: AF-143-2/EC-3917

Test Temperature (°F)	(°C)	Pre-Test Conditioning [Days @ 140°F(60°C) and 95-100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh.Failure)
72	22	None	6160	42.5	100
72	22	None	6390	44.1	100
72	22	None	6490	44.7	100
72	22	None	6140	42.3	50
72	22	None	6550	45.2	100
72	22	None	6270	43.2	75
Average			6330	43.6	85
Std. Dev.			148	1.0	0
140	60	None	5170	35.6	100
140	60	None	5150	35.5	60
140	60	None	5170	35.6	90
140	60	None	5170	35.6	100
140	60	None	5180	35.7	100
140	60	None	5190	35.8	100
140	60	None	5190	35.8	100
140	60	None	5190	35.8	100
140	60	None	5210	35.9	100
140	60	None	5200	35.8	100
Average			5180	35.7	95
Std. Dev.			21	0.2	0
250	121	None	4320	29.8	100
250	121	None	4230	29.2	100
250	121	None	4410	30.4	100
250	121	None	4310	29.7	100
250	121	None	4550	31.4	100
250	121	None	4310	29.7	90
Average			4355	30.0	100
Std. Dev.			111	0.8	0
72	22	30	5970	41.2	100
72	22	30	6150	42.4	100
72	22	30	6150	42.4	100
72	22	30	5970	41.2	100
72	22	30	5810	40.1	100
72	22	30	5790	40.0	100
Average			5970	41.2	100
Std. Dev.			158	1.1	0
72	22	100	5770	39.8	100
72	22	100	5890	40.6	100
72	22	100	5650	39.0	100
72	22	100	5750	39.6	100
72	22	100	5830	40.2	100
Average			5780	39.8	100
Std. Dev.			90	0.6	0

TABLE A.4

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728

Test Temperature (°F)	(°C)	Pre-Test Conditioning [days @ 140°F(60°C) and 95-100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh.Failure)
72	22	None	3710	25.6	100
72	22	None	4250	29.3	100
72	22	None	4000	27.6	100
72	22	None	3580	24.7	100
72	22	None	4040	27.9	100
Average			3920	27.0	100
Std. Dev.			268	1.8	0
140	60	None	3260	22.5	100
140	60	None	4070	28.1	100
140	60	None	3870	26.7	100
140	60	None	3860	26.6	100
140	60	None	3750	25.9	100
140	60	None	3740	25.8	100
140	60	None	4050	27.9	100
140	60	None	4110	28.3	100
140	60	None	4360	30.1	100
140	60	None	3520	24.3	100
140	60	None	4430	30.5	100
Average			3910	27.0	100
Std. Dev.			345	2.4	0
250	121	None	3700	25.5	100
250	121	None	3620	25.0	100
250	121	None	3420	23.6	100
250	121	None	3100	21.4	100
250	121	None	3050	21.0	100
Average			3380	23.3	100
Std. Dev.			295	2.0	0
72	22	28	3270	22.5	100
72	22	28	3230	22.3	100
72	22	28	2720	18.8	100
72	22	28	3060	21.1	100
72	22	28	2970	20.5	100
Average			3050	21.0	100
Std. Dev.			221	1.5	0

TABLE A.5

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728

Test Temperature (°F)	(°C)	Pre-Test Conditioning [Days @ 140°F(60°C) and 95-100% R.H.; No Load]	Ultimate Strength (psi)	(MPa)	Failure Mode (% Coh.Failure)
72	22	None	5740	39.6	100
72	22	None	5730	39.5	100
72	22	None	5900	40.7	100
72	22	None	6380	44.0	100
72	22	None	6550	45.2	100
72	22	None	7360	50.7	100
72	22	None	6870	47.4	100
72	22	None	6440	44.4	100
72	22	None	6420	44.3	100
72	22	None	6320	43.6	100
Average			6370	43.9	100
Std. Dev.			505	3.5	0
140	60	None	6260	43.2	100
140	60	None	6060	41.8	100
140	60	None	6270	43.2	100
140	60	None	5860	40.4	100
140	60	None	4480	30.9	100
Average			5780	39.8	100
Std. Dev.			757	5.2	0
250	121	None	4770	32.9	100
250	121	None	5010	34.5	100
250	121	None	5050	34.8	100
250	121	None	4770	32.9	100
250	121	None	4260	29.4	100
Average			4770	32.9	100
Std. Dev.			314	2.2	0
72	22	28	6200	42.7	100
72	22	28	6650	45.8	75
72	22	28	7290	50.3	100
72	22	28	6880	47.4	100
72	22	28	5790	39.9	50
Average			6560	45.2	85
Std. Dev.			585	4.0	0
72	22	100	5820	40.1	100
72	22	100	6500	44.8	90
72	22	100	6730	46.4	90
Average			6350	43.8	95
Std. Dev.			476	3.3	0

TABLE A.6

SINGLE LAP SHEAR STRENGTH OF ADHESIVE JOINTS

Adherend Alloy: 7075 T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: PL-729-3/PL-728

Test Temperature (°F)	Test Temperature (°C)	Pre-Test Conditioning [days @ 140°F(60°C) and 95-100% R.H.; No Load]	Ultimate Strength (psi)	Ultimate Strength (MPa)	Failure Mode[1] (% Coh.Failure)
72	22	None	6500	44.8	0
72	22	None	6950	47.9	0
72	22	None	6070	41.8	0
72	22	None	7220	49.8	0
72	22	None	5970	41.2	0
72	22	None	6730	46.4	0
Average			6570	45.3	0
Std. Dev.			491.4	3.4	0
140	60	None	6370	43.9	0
140	60	None	6490	44.7	0
140	60	None	6190	42.7	0
140	60	None	6290	43.4	0
140	60	None	5790	39.9	0
140	60	None	6110	42.1	0
140	60	None	6380	44.0	0
140	60	None	6390	44.1	0
140	60	None	6310	43.5	0
140	60	None	6390	44.1	0
140	60	None	6340	43.7	0
Average			6280	43.3	0
Std. Dev.			397	2.7	0
250	121	None	4470	30.8	0
250	121	None	4420	30.5	0
250	121	None	4720	32.5	0
250	121	None	4420	30.5	0
250	121	None	4520	31.2	0
250	121	None	4460	30.7	0
Average			4500	31.0	0
Std. Dev.			113.2	0.8	0
72	22	30	7250	49.9	0
72	22	30	7090	48.9	0
72	22	30	7240	49.9	0
72	22	30	7180	49.5	0
72	22	30	7180	49.5	0
72	22	30	7190	49.6	0
Average			7180	49.5	0
Std. Dev.			95	0.7	0
72	22	100	8320	57.3	0
72	22	100	7240	49.9	0
72	22	100	7260	50.0	0
72	22	100	6350	43.8	0
72	22	100	6260	43.1	0
72	22	100	8290	57.1	0
Average			7290	50.3	0
Std. Dev.			895	6.2	0

[1]All failure modes in this table were adhesive, along the adhesive/primer interface.

TABLE A.7

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: AF-143-2/EC-3917
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 72°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Strength (psi)	(MPa)	Failure Mode (% Coh.)
2420	16.7	80	0.30	---	---	100
2420	16.7	80	0.50	---	---	100
2420	16.7	80	1.25	---	---	100
Average			0.68	---	---	100
Std. Dev.			0.50	---	---	0
2110	14.6	70	150	---	---	100
2110	14.6	70	2400	3340	23.0	100
2110	14.6	70	2400	3130	21.6	100
Average			1650	3250	22.4	100
Std. Dev.			1300	110	0.7	0
1810	12.5	60	2400	3100	21.4	100
1810	12.5	60	2400	2990	20.6	100
1810	12.5	60	2400	2950	20.3	100
Average			2400	3010	20.8	100
Std. Dev.			0	80	0.5	0
1510	10.4	50	2400	3050	21.0	100
1510	10.4	50	2400	3170	21.9	100
1510	10.4	50	2400	3050	21.0	100
Average			2400	3090	21.3	100
Std. Dev.			0	70	0.5	0
600	4.1	20	2400	3090	21.3	100
600	4.1	20	2400	2800	19.3	100
600	4.1	20	2400	2760	19.0	100
Average			2400	2880	19.9	100
Std. Dev.			0	180	1.3	0

TABLE A.8

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy:	2024 T3 Bare
Adherend Thickness:	0.250 inch (0.64 cm)
Surface Preparation:	Optimized FPL Etch
Adhesive/Primer:	AF-143-2/EC-3917
Exposure Environment:	140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Strength (psi)	(MPa)	Failure Mode (% Coh.)
3920	27.0	80	4	---	---	100
3920	27.0	80	3.4	---	---	100
3920	27.0	80	0.3	---	---	100
Average			2.6	---	---	100
Std. Dev.			2.0	---	---	0
3430	23.7	70	155	---	---	100
3430	23.7	70	555	---	---	100
3430	23.7	70	370	---	---	100
3430	23.7	70	282	---	---	100
Average			340	---	---	100
Std. Dev.			170	---	---	0
3180	21.9	65	370	---	---	100
3180	21.9	65	450	---	---	100
3180	21.9	65	820	---	---	100
3180	21.9	65	433	---	---	100
Average			480	---	---	100
Std. Dev.			200	---	---	0
2940	20.3	60	985	---	---	100
2940	20.3	60	940	---	---	100
2940	20.3	60	1210	---	---	100
Average			1043	---	---	100
Std. Dev.			145	---	---	0
1960	13.5	40	2400	5800	40.0	100
1960	13.5	40	2400	5740	39.6	100
1960	13.5	40	2400	5620	38.7	100
Average			2400	5720	39.4	100
Std. Dev.			0	90	0.6	0
980	6.8	20	2400	5590	38.5	100
980	6.8	20	2400	5790	39.9	100
980	6.8	20	2400	5030	34.7	100
Average			2400	5470	37.7	100
Std. Dev.			0	400	2.8	0

TABLE A.9

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 7075 T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: AF-143-2/EC-3917
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Strength (psi)	(MPa)	Failure Mode (% Coh.)
3630	25.0	70	400	---	---	100
3630	25.0	70	370	---	---	100
3630	25.0	70	680	---	---	100
Average			480	---	---	100
Std. Dev.			170	---	---	0
3110	21.4	60	2320	---	---	100
3110	21.4	60	1740	---	---	100
3110	21.4	60	530	---	---	100
Average			1530	---	---	100
Std. Dev.			910	---	---	0
2590	17.6	50	2400	2680	18.5	100
2590	17.6	50	2400	5860	40.4	100
Average			2400	4270	29.5	100
Std. Dev.			0	---	---	0
2070	14.3	40	2400	5800	40.0	100
2070	14.3	40	2400	5940	41.0	100
2070	14.3	40	2400	5950	41.0	100
Average			2400	5900	40.7	100
Std. Dev.			0	80	0.6	0
1550	10.7	30	2400	5820	40.1	100
1550	10.7	30	2400	5650	40.0	100
1550	10.7	30	2400	5830	40.2	100
Average			2400	5760	39.7	100
Std. Dev.			0	90	0.6	0
1040	7.2	20	2400	5910	40.7	100
1040	7.2	20	2400	5710	39.4	100
1040	7.2	20	2400	5890	40.6	100
Average			2400	5840	40.3	100
Std. Dev.			0	110	0.8	0

TABLE A.10

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.063 inch (0.16 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 72°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Strength (psi)	(MPa)	Failure Mode (% Coh.)
2740	18.9	70	8.9	---	---	100
2740	18.9	70	2400	3610	24.9	100
2740	18.9	70	44.9	---	---	100
2740	18.9	70	88.8	---	---	100
2740	18.9	70	1.3	---	---	100
Average			510	---	---	100
Std. Dev.			1060	---	---	0
2350	16.2	60	2400	3720	25.6	100
2350	16.2	60	2400	3720	25.6	100
2350	16.2	60	1160	---	---	100
Average			1990	3720	25.6	100
Std. Dev.			720	0	0	0
1960	13.5	50	2400	4310	29.7	100
1960	13.5	50	2400	3900	26.9	100
1960	13.5	50	2400	3780	26.1	100
Average			2400	4000	27.6	100
Std. Dev.			0	280	1.9	0
780	5.4	20	2400	3940	27.2	100
780	5.4	20	2400	4010	27.6	100
780	5.4	20	2400	3140	21.6	100
Average			2400	3700	25.5	100
Std. Dev.			0	480	3.4	0

TABLE A.11

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 2024 T3 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Optimized FPL Etch
Adhesive/Primer: PL-729-3/PL-728
Exposure Environment: 140°F(60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	(% of 140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Strength (psi)	(MPa)	Failure Mode (% Coh.)
4630	31.9	80	21.0	---	---	100
4630	31.9	80	18.4	---	---	100
4630	31.9	80	7.7	---	---	100
Average			15.7	---	---	100
Std. Dev.			7.0	---	---	0
4050	27.9	70	1010	---	---	100
4050	27.9	70	245	---	---	90
4050	27.9	70	590	---	---	100
Average			615	---	---	95
Std. Dev.			380	---	---	6
3760	25.9	65	480	---	---	90
3760	25.9	65	1220	---	---	100
3760	25.9	65	760	---	---	90
Average			820	---	---	90
Std. Dev.			370	---	---	6
3470	23.9	60	760	---	---	25
3470	23.9	60	1020	---	---	100
3470	23.9	60	650	---	---	75
Average			810	---	---	70
Std. Dev.			190	---	---	40
2330	16.1	40	2400	5720	39.4	60
2330	16.1	40	2400	5540	38.2	60
2330	16.1	40	780	---	---	50
Average			1860	5630	38.8	55
Std. Dev.			940	130	0.9	6
1160	4.0	20	2400	6670	46.0	90
1160	4.0	20	2400	6620	45.6	100
1160	4.0	20	2400	6700	46.2	80
Average			2400	6660	45.9	90
Std. Dev.			0	40	0.3	10

TABLE A.12

ENVIRONMENTAL STRESS-RUPTURE LAP SHEAR BEHAVIOR OF ADHESIVE JOINTS

Adherend Alloy: 7075 T6 Bare
Adherend Thickness: 0.250 inch (0.64 cm)
Surface Preparation: Phosphoric Acid Anodized
Adhesive/Primer: PL-729-3/PL-728
Exposure Environment: 140°F (60°C) and 95-100% R.H.

Joint Shear Stress During Exposure (psi)	(MPa)	% of (140°F dry ultimate)	Time to Failure (hrs)	Residual Lap Shear Strength (psi)	(MPa)	Failure Mode[1] (% Coh.)
3770	26.0	60	810	---	---	0
3770	26.0	60	2400	6460	44.5	0
3770	26.0	60	1800	6400	44.1	0
Average			1670	6430	44.3	0
Std. Dev.			800	44	0.3	0
3140	21.6	50	1700	6220	42.9	0
2510	17.3	40	2400	5900	47.6	0
2510	17.3	40	2400	7500	57.7	0
2510	17.3	40	2400	6820	47.0	0
Average			2400	7070	48.7	0
Std. Dev.			0	370	2.6	0
1880	13.0	30	2400	7960	54.9	0
1880	13.0	30	2400	7170	49.4	0
1880	13.0	30	2400	6420	44.3	0
Average			2400	7180	49.5	0
Std. Dev.			0	770	5.3	0
1260	8.7	20	2400	7660	52.8	0
1260	8.7	20	2400	5830	40.2	0
1260	8.7	20	2400	7420	51.2	0
Average			2400	6970	48.1	0
Std. Dev.			0	990	6.9	0

[1]All failure modes in this table were adhesive, along the adhesive/primer interface.

APPENDIX B

ESCA FRACTURE SURFACE ANALYSIS OF PL-729 BONDS ON 7075 ADHERENDS

APPENDIX B

ESCA FRACTURE SURFACE ANALYSIS OF PL-729 BONDS ON 7075 ADHERENDS

We have examined the following samples with ESCA (Electron Spectroscopy for Chemical Analysis):

1. Adhesive: PL-729
2. Primer: PL-728
3. R.T. Lap Shear Fracture Surfaces
4. 140°F Lap Shear Fracture Surfaces
5. 250°F Lap Shear Fracture Surfaces.

Each specimen prior to analysis was given ten analytical wipes with methanol. The last three specimens contained two faces as a result of the lap shear test. One face was yellow (adhesive color) and the other was gray in color.

Figures B.1 and B.2 illustrate the overall ESCA spectra for the adhesive and primer, respectively. From these scans a qualitative analysis can be made of the adhesive and primer. As can be seen from these figures, the major elements composing the adhesive and primer are C and O. Smaller amounts of nitrogen and sulfur can also be noted. Table B.1 summarizes the quantitative results obtained by ESCA on the adhesive and primer.

TABLE B.1

QUANTITATIVE ANALYSIS OF PRIMER AND ADHESIVE

Element	ESCA Level	Binding Energy (eV)	Atomic % Adhesive	Atomic % Primer
Carbon	1s	285.0	60.3	60.1
		286.8	26.2	24.8
Oxygen	1s	532.1	11.3	12.3
Nitrogen	1s	399.4	2.1	2.8

The data in the table illustrate that the primer contains ∿9% greater oxygen concentration than the adhesive and ∿25%

greater nitrogen. Sulfur in these specimens was determined to be ~1 atomic percent.

The surfaces of the lap shear specimens where fracture occurred contain, in addition to C, O, N, and S, contaminant elements Cl and, in particular, Si. Figures B.3, B.4, and B.5 illustrate the ESCA overall scans of these fractured surfaces.

TABLE B.2

QUANTITATIVE ANALYSIS OF FRACTURED SURFACES

Element	ESCA Level	Binding Energy (eV)	R.T. Atomic % Yellow	R.T. Atomic % Gray	140°F Atomic % Yellow	140°F Atomic % Gray	250°F Atomic % Yellow	250°F Atomic % Gray	Adh.	Primer
Carbon	1s	295.0	67.7	58.4	65.3	63.4	61.8	63.5	60.3	60.1
	1s	286.8	13.7	21.5	20.2	18.0	18.6	19.8	26.2	24.3
Oxygen	1s	533.2	17.2	17.2	12.6	14.4	16.5	14.2	11.3	12.3
Nitrogen	1s	400.2	1.4	2.8	1.9	2.2	3.1	2.5	2.1	2.8

Comparing the oxygen amount noted in Table B.2 vs. that measured in Table B.1, we see that the oxygen concentration is larger on the fractured surface. Could there be SiO_2 particles migrating to the fractured surfaces due to filler materials? The atomic percentages of both the "yellow" and "gray" fracture surfaces approximate the composition of the primer itself. These data suggest a possible failure mode occurring within the primer.

In summary, the preliminary results obtained with ESCA on the mode of fracture with lap shear specimens show:

1. Contaminant elements, Si and Cl, at the fractured surfaces, and

2. The fracture surfaces appear similar, in atomic percent, to that of the neat primer.

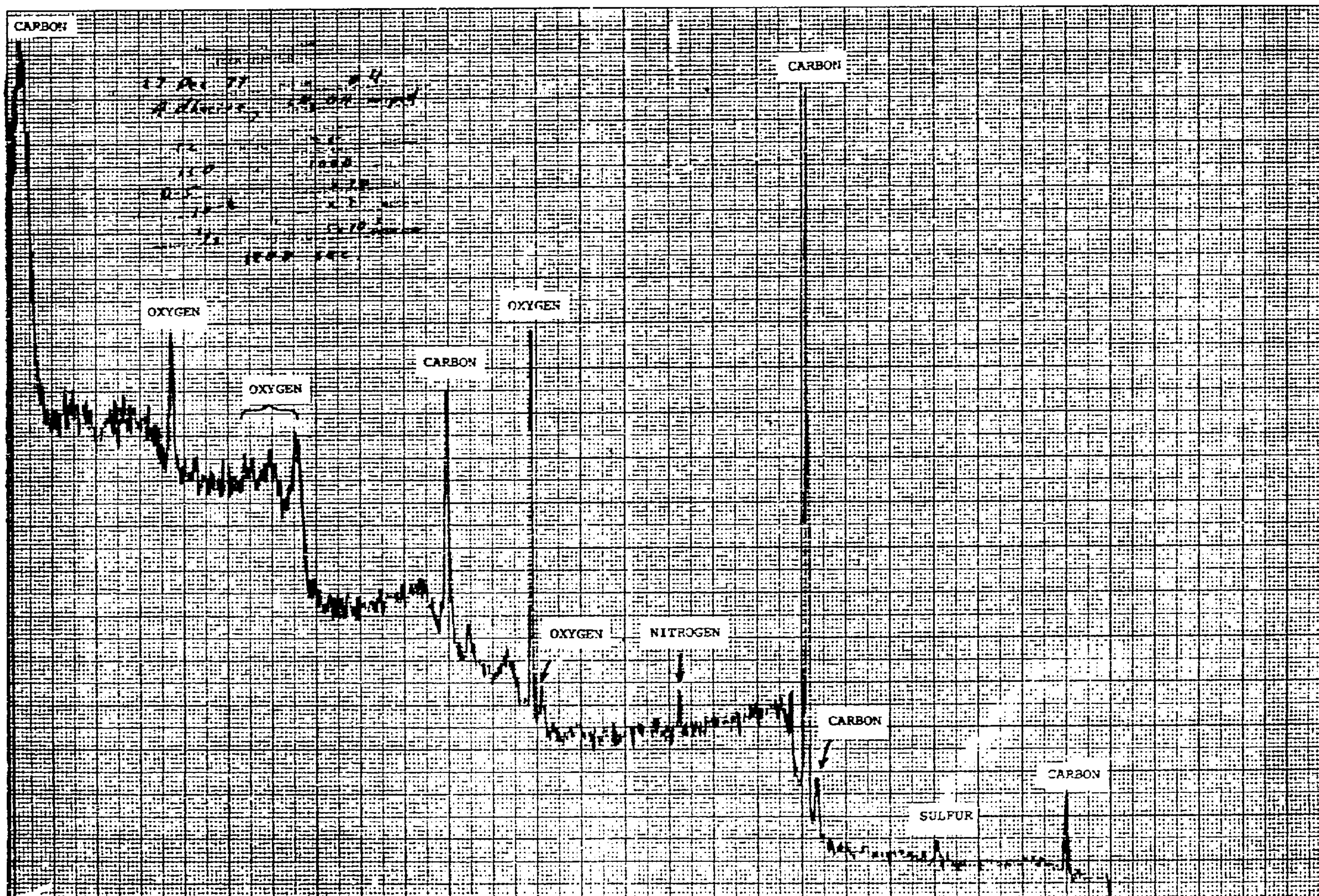

Figure B.1. Overall ESCA Spectrum of Adhesive.

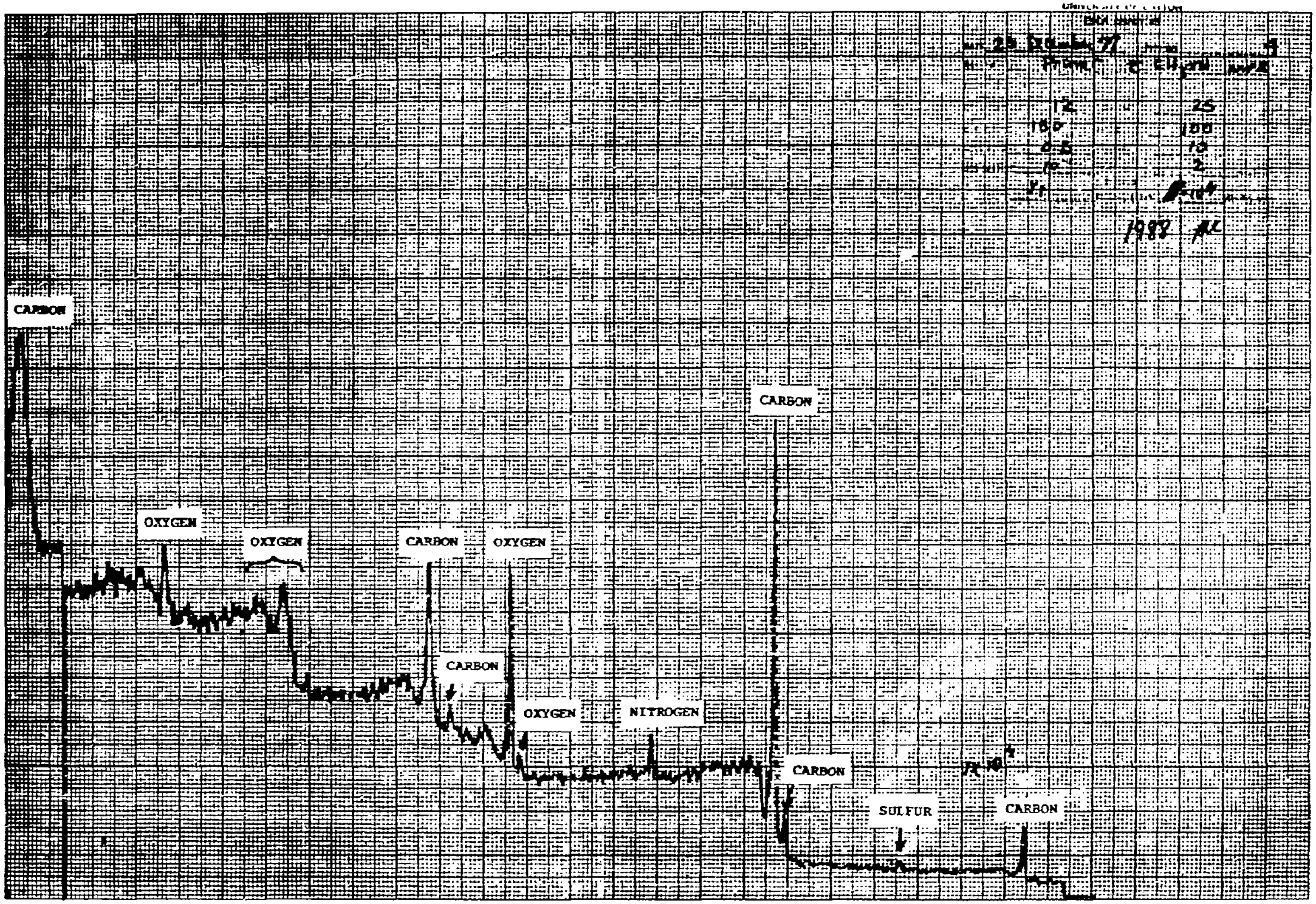

Figure B.2. Overall ESCA Spectrum of Primer.

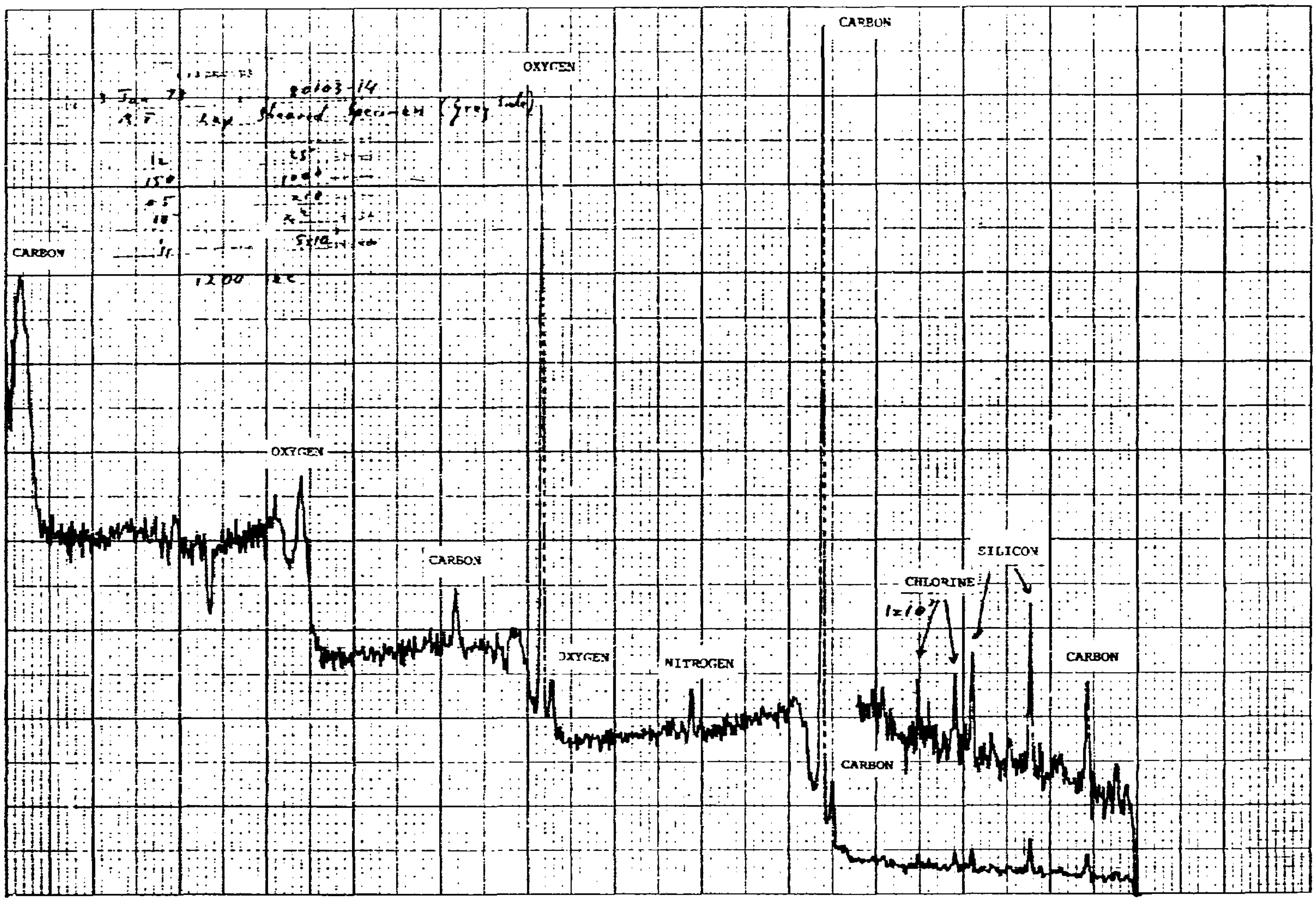

Figure B.3a. Overall ESCA Spectrum of R.T. Lap Sheared Specimen (gray side).

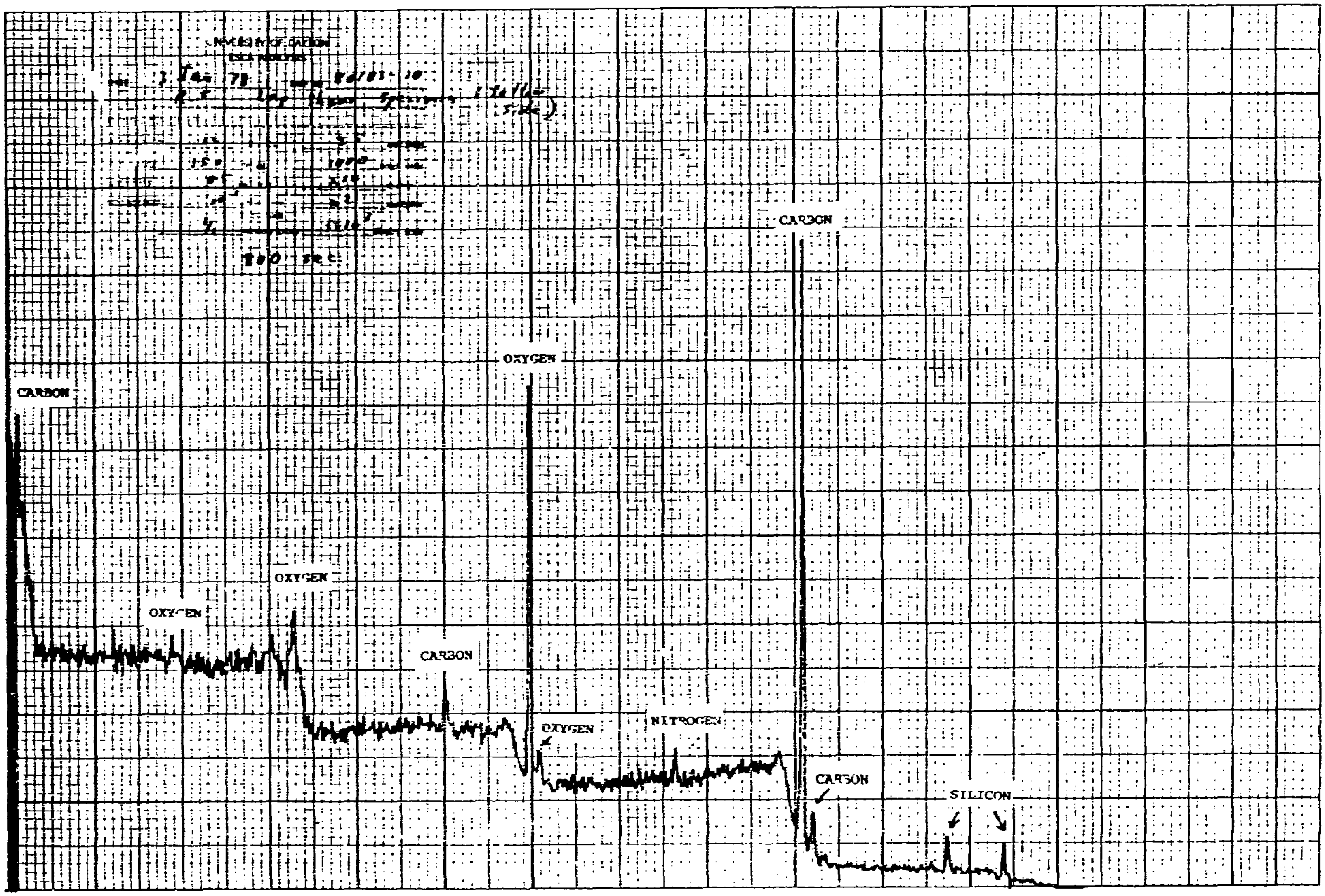

Figure B.3b. Overall ESCA Spectrum of R.T. Lap Sheared Specimen (yellow side).

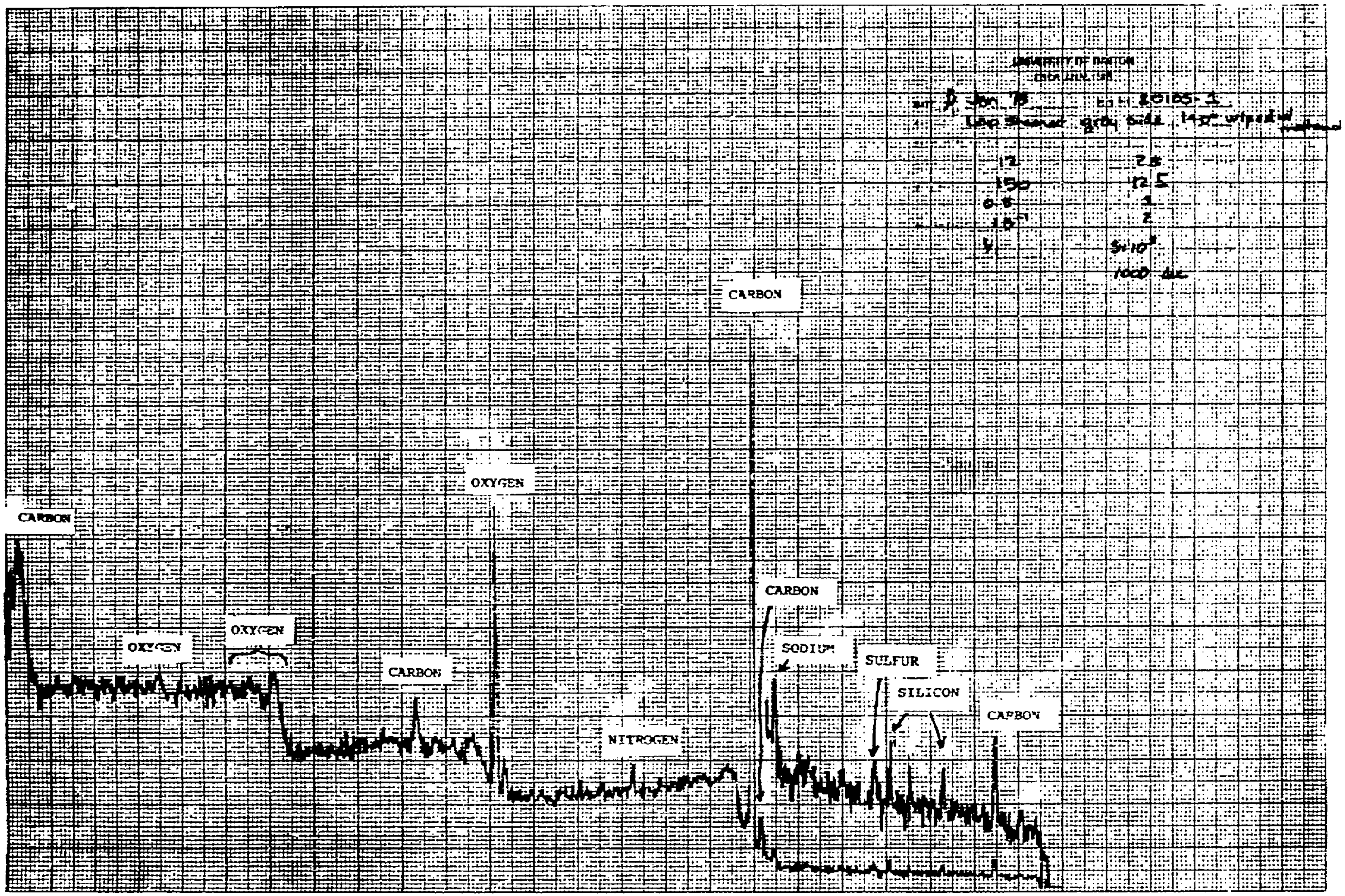

Figure B.4a. Overall ESCA Spectrum of 140°F (60°C) Lap Sheared Specimen (gray side).

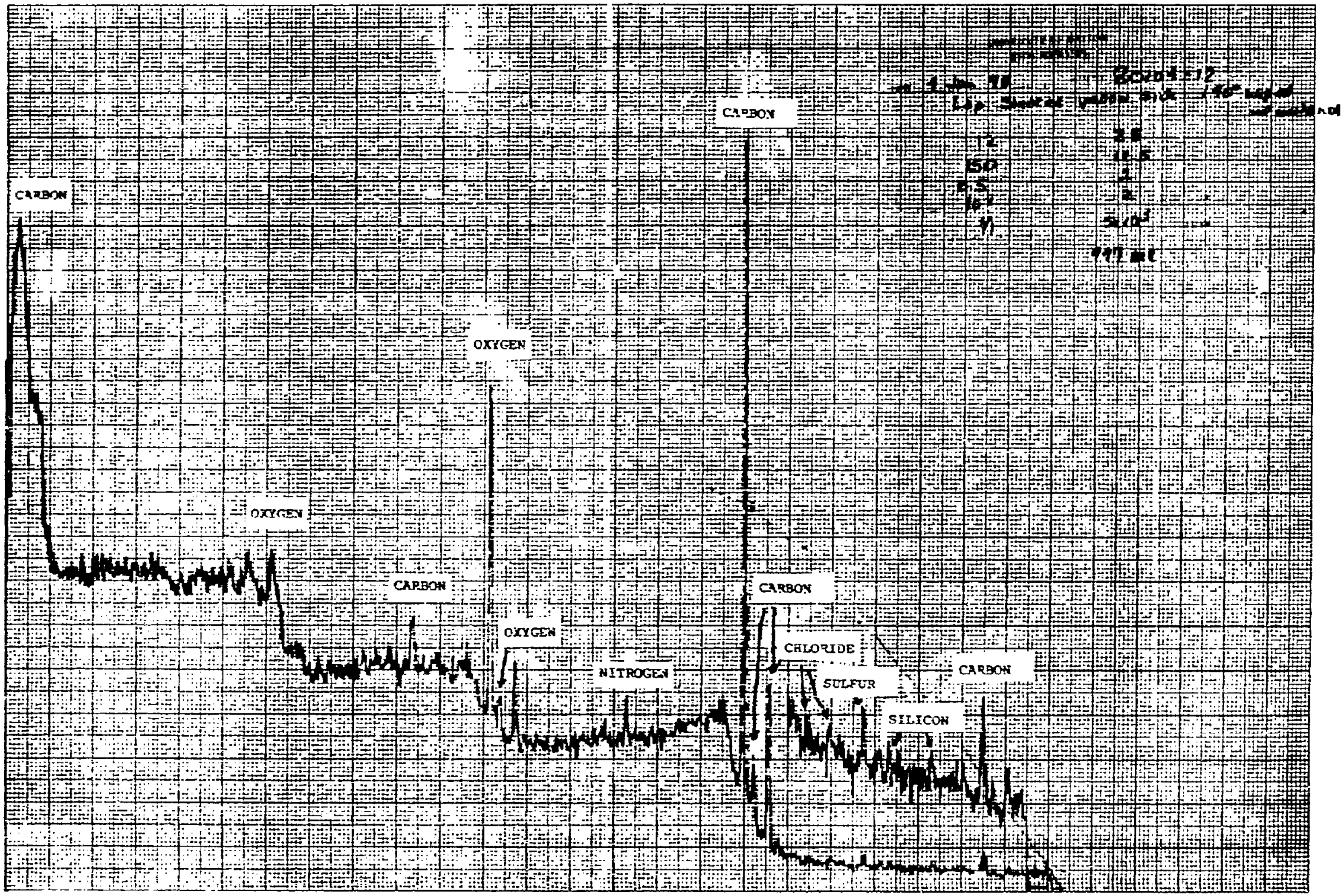

Figure B.4b. Overall ESCA Spectrum of 140°F (60°C) Lap Sheared Specimen (yellow side).

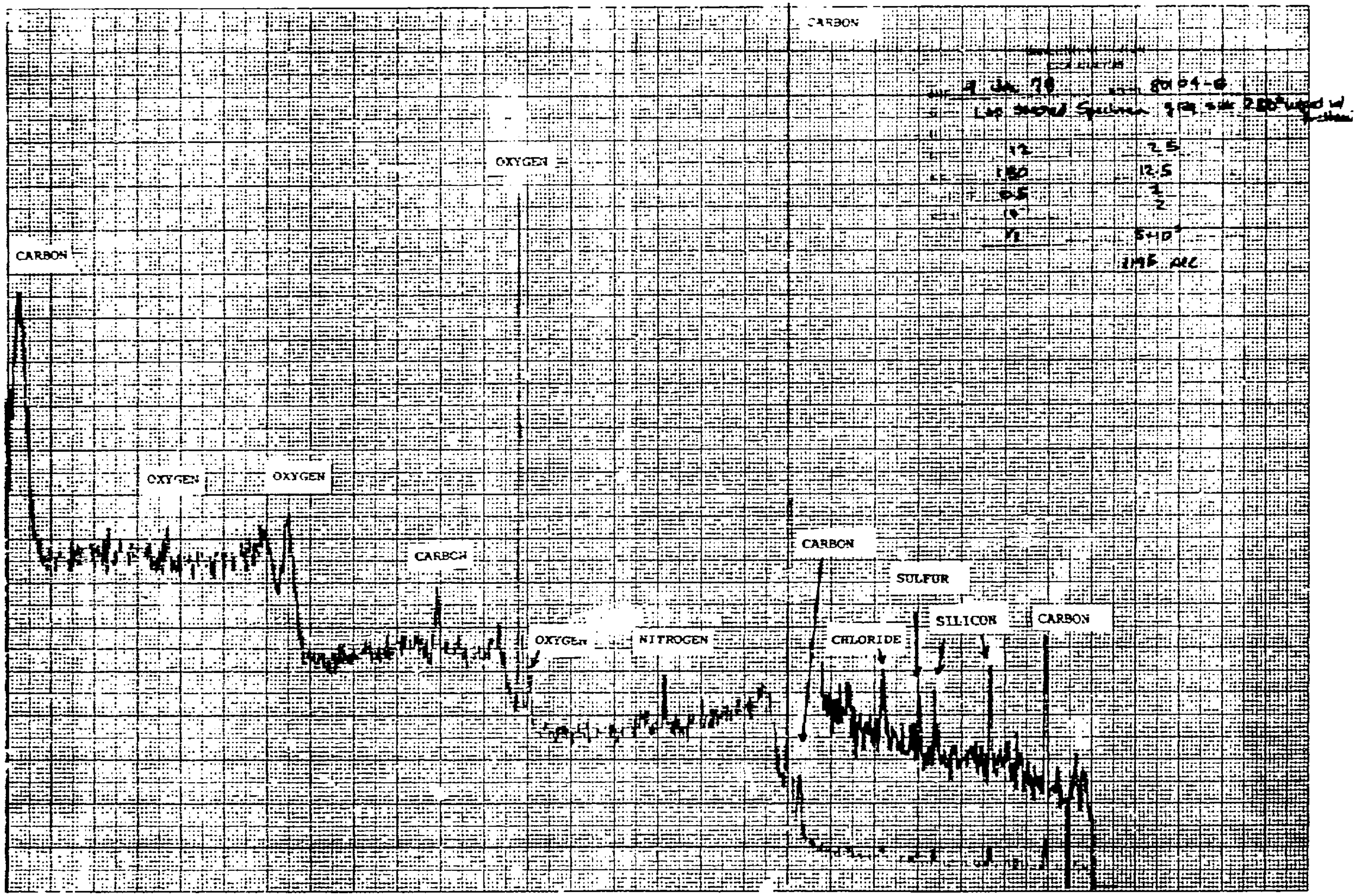

Figure B.5a. Overall ESCA Spectrum of 250°F (121°C) Lap Sheared Specimen (gray side).

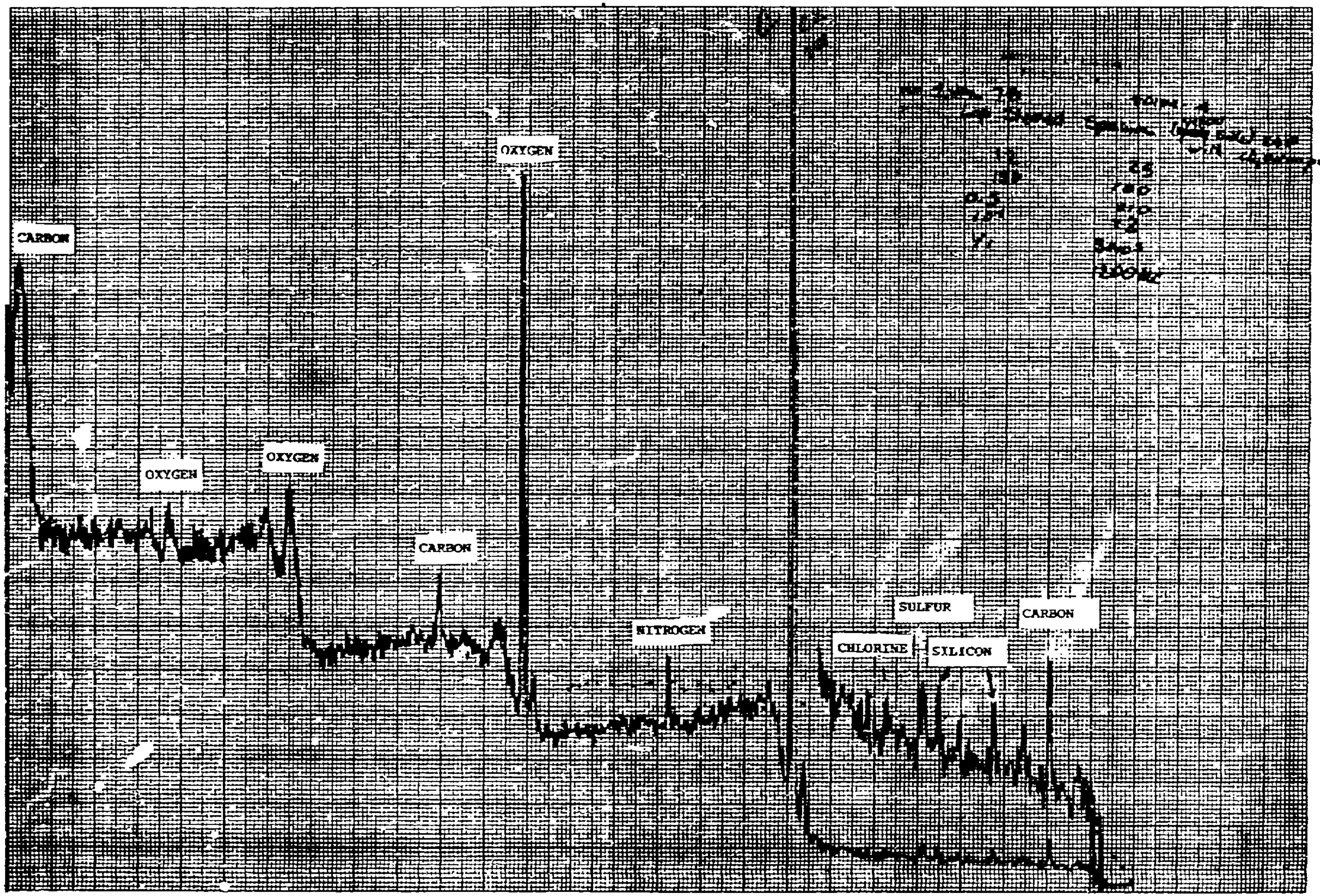

Figure B.5b. Overall ESCA Spectrum of 250°F (121°C) Lap Sheared Specimen (yellow side).

APPENDIX C

CHARACTERISTICS OF AF-143 AND PL-729 ADHESIVES

APPENDIX C

CHARACTERISTICS OF AF-143 AND PL-729 ADHESIVES*

AF-143

Composition	phr	% w
Nylon scrim cloth		2.5
Adhesive		
Carbide ERL 0510, V	100	97.5
Diaminodiphenylsulfone, VIII	39	
Dicyandiamide, X	1.5	
Crosslinked elastomer	24	
Asbestos filler	13	

Component Atomic Compositions

N-N,Diglycidyl-P-Aminophenylglycidyl Ether, V (ERL 0510, TGPAP)	$C_{15}H_{19}O_4N$
Diaminodiphenylsulfone, VIII (CIBA Eporal, DDS)	$C_{12}H_{12}O_2N_2S$
Dicyanidiamide, X (DICY)	$C_2H_5N_4$
Asbestos	$Ca_2Mg_5Si_8O_{22}(OH)_2$ [approximate]

*Communication from H. Schwartz, USAF Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

PL-729

Composition	phr	% w
Nylon Scrim Carrier		2.4
Adhesive		
Carbide ERL 0510, V (or equivalent)	50	97.6
Shell EPON 828, III (or equivalent)	50	
Carboxy terminated nitrile elastomer	5-20	
Diaminodiphenylsulfone, VIII	32	
Asbestos type filler	1.5	

Component Atomic Compositions

N,N-Diglycidyl-P-Aminophenylglycidyl Ether, V (ERL 0510, TGPAP)	$C_{15}H_{19}O_4N$
Diglycidyl Ether of Bisphenol A, III (Epon 828, DGEBPA)	$C_{21}H_{24}O_4$
Diaminodiphenylsulfone, VIII (CIBA Eporal, DDS)	$C_{12}H_{12}O_2N_2S$
Asbestos	$Ca_2Mg_5Si_8O_{22}(OH)_2$ [approximate]

APPENDIX D

COMPUTATION OF STRESS/STRAIN IN ADHEREND SURFACE OXIDE

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In view of the environmental stress-rupture time-to-failure behavior illustrated in Figure 11 and discussed in Section IV.2, it was decided to try to determine if the 2800 psi (1.93 MPa) shear stress level at which the curves for the two adhesives diverge corresponds to the point at which the aluminum oxide adherend surface layers might be fracturing. In order not to confuse the illustrated calculations, they will be presented utilizing the widely recognized English units and the metric (SI) equivalents will only be given in parentheses for the final, computed quantities.

Step 1. Computation of Load on Specimen

The lap joints utilized during this investigation were 1 inch (2.54 cm) wide with a 0.5 inch (1.27 cm) overlap, giving a shear area of 0.5 $inch^2$ (3.23 cm^2). Hence, for a 2800 psi (1.93 MPa) shear stress:

$$\tau = \frac{P}{A},$$

where:

τ = 2800 psi

A = 0.50 in^2

P = load (lbs).

$$P = \tau A = 2800(0.50) = 1400 \text{ lbs} (6227 \text{ N})$$

Step 2. Computation of Strain in Adherend and Adherend Surface Oxide Layer

The adherends (illustrated in Figure 4.b) each had cross-sectional dimensions of 1 inch (2.54 cm) wide by 0.25 inch (0.63 cm) thick, giving a cross-sectional area of 0.25 $inch^2$ (1.60 cm^2). Hence, for a tensile load of 1400 lbs (6227 N) in the adherend:

$$\sigma = \frac{P}{A},$$

where:

σ = tensile stress (psi)

P = tensile load (lbs)

A = cross-sectional area (in^2).

$$\sigma = \frac{1400}{0.25} = 5600 \text{ psi } (38.6 \text{ MPa})$$

Since, for aluminum: $E = 10.6 \times 10^6$ psi

and $\varepsilon = \frac{\sigma}{E},$

$$\varepsilon = \frac{5600}{10.6 \times 10^6} = 5.3 \times 10^{-4} \text{ in/in } (5.3 \times 10^{-4} \text{ cm/cm}) \text{ strain}$$

Step 3. Comparison of Al_2O_3 Failure Properties With Computed Strain

While it is recognized that the stress on the adherend surface varies along the length of the lap joint, and further that, even with thick adherends one still encounters bending stresses at the ends of single lap joints, the computations presented here at least give some idea of the likelihood of the oxide undergoing fracture at the shear stress level of interest. Adding to the two factors above, the exact crystalline nature and orientation within the surface oxide layer are unknown. At any rate, generally accepted values* for Al_2O_3 properties are:

$E = 55\text{-}60 \times 10^6$ psi ($3.8\text{-}4.1 \times 10^5$ MPa)

$\sigma_{UTS} = 35\text{-}40 \times 10^3$ psi (0.24-0.27 MPa)

$\varepsilon_{UTS} \doteq 6.2 \times 10^{-4}$ in/in (6.7×10^{-4} cm/cm).

Comparison of the ultimate tensile strain with the computed strain indicates that the computed strain is only 15% below that needed for fracture. Considering the presence of the bending

*Engineering Properties of Selected Ceramic Materials; American Ceramic Society, Columbus, Ohio, 1966.

stresses, the differences between bulk Al_2O_3 and the Al_2O_3 on the adherend surfaces, and further, the susceptibility of Al_2O_3 to static fatigue in the presence of water or humidity, it is very reasonable to expect that at this stress level the surface oxide film develops fracture cracks during the environmental stress-rupture tests.

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